Nutrient Flux Study

Results From the Murderkill River – Marsh Ecosystem

Final Report

Kent County Levy Court

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From

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EXECUTIVE SUMMARY

In July 2007 and April 2008 sites were sampled for biogeochemical fluxes from the Murderkill River/Wetland ecosystem, with an understanding of nitrogen sinks in the ecosystem as the major study focus. The final data set included:

- Subtidal measurements of sediment-water exchange in the river during July 2007
- Small creek and marsh sediment-water exchange in July 2007
- Small creek and marsh sediment-water exchange in April 2008
- Experiments on the effect of nitrate additions to the marsh in July 2007
- Sediment geochronology and nutrient burial estimates at two sites.

The key finding of the sediment-water exchange and nutrient burial studies were:

- Denitrification occurs at high rates throughout this ecosystem, with the potential of removing a high proportion of the incoming nitrogen

- Nitrogen burial is also an important nitrogen sink, with rates similar to that of denitrification

- Sediment denitrification increased quickly with the addition of nitrate

In addition to sediment studies, water column respiration was measured on two occasions using high precision membrane inlet mass spectrometry. Key findings were:

- The Murderkill River water column respiration rates measured in April and July 2008 averaged 1.2+/-0.5 and 1.5+/-0.3 respectively
-
- Nitrification is an important process consuming O_2 in the water column of the Murderkill River and at times accounts for 50% of the O_2 consumption

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ACKNOWLEDGEMENTS

Funding for this project was provided by the Kent County Levy Court, with Hans Medlarz of Kent County and Mirsajadi Hassan at DNREC guiding the content of this assessment program. We are grateful for the opportunity to apply our biogeochemical measurements across the salinity gradient in such an extensive and environmentally-important wetland. The water column oxygen flux project was done in cooperation with Jon Sharp at the University of Delaware.

SECTION I: WETLAND NITROGEN CYCLING

INTRODUCTION

Sediment flux studies were carried out in July 2007 and April 2008 for both subtidal and marsh environments. A synopsis of the study questions/approach from our proposal is below:

> *The goal of this work is to use state of the art techniques to provide the highest quality sediment-water exchange data possible; included in these fluxes are measurements of denitrification. The focus of this work is on sediment processes that 1) remove oxygen from surface water, 2) result in the uptake or release of N and P, and 3) are long-term sinks of N and P (i.e. burial – (Merrill and Cornwell 2000); denitrification – (Cornwell et al. 1999)). Sediment-water exchange measurements will be made on triplicate cores from a total of 6 study sites at 2 times of the year (July 2007 and April 2008) with an additional 4 study sites distributed over the mainstem of the river in July 2007. The data from these studies will be presented in a data report after each sampling trip followed by an interpretive summary report at the end of the project.*

This report presents the data from this project with a view towards 1) how Murderkill River marshes process N and P and 2) how the rates/observation compare with comparable marsh sites in the mid-Atlantic area. Our project consisted of:

- Subtidal fluxes at 4 sites (triplicate cores) in the tidal mainstem river (2007)
- Triplicate core incubations at 6 other sites in 2007 and 2008. Each "site" consisted of a subtidal core from a small creek, and single cores from the marsh environment on opposite sides of the creek.
- ^{210}Pb analyses for sedimentation rates with concurrent N and P concentration information

We are pleased with this project's flux data; it appears to be of the highest quality and is readily interpreted. Part of the success relative to some of our other marsh studies (Merrill 1999; Merrill and Cornwell 2000; Greene 2005) comes from the relatively fine-grained inorganic nature of the soil in the marshes. Our sample time corresponded to times of the year with higher nitrate and lower salinity (April 2008) and lower nitrate plus higher salinity (July 2007).

A second study examining water column respiration is included as an appendix to this report on marsh N cycling. Water column oxygen respiration was measured on two occasions.

DESCRIPTION OF STUDY SITES

Sites 1-4 progress upstream from the Delaware Bay end of the Murderkill River (Table 1: Figure 1). These 4 sites were used for collection of sediment from the mainstem Murderkill River; samples were collected on July 19, 2007. The shallow subtidal/marsh transect was sampled on July 23, 2007 and April 27, 2008, with stations 5-10 progressing up river. Of special note is site 8, in the creek receiving treated water from the Kent County facility.

Table 1. Station locations and site water chemistry

ID	Date	Lat N	Long W	Depth	T	S	DO	pH	NH_4^+	SRP	NO_{2+3}^-
				m	°C		mg L^{-1}		μmol L-1		
	Summer 2007 Main River Flux Cores										
1	07-19-07	39°02.854	75°23.613	2.9	27.55	19.8	4.62	6.91	3.24	1.42	9.1
2	07-19-07	39°01.251	75°25.467	3.4	27.89	11.5	3.93	6.75	4.64	4.00	20.0
3	07-19-07	39°00.592	75°26.383	2.8	28.04	10.4	3.94	6.68	17.8	3.64	21.8
4	07-19-07	39°00.718	75°27.099	1.5	28.17	7.4	4.42	6.55	11.8	3.16	28.0
	Summer 2007 Creek Flux Cores										
5	07-23-07	39°03.039	75°23.427	0.2	24.77	20.4	6.24	7.55	6.70	0.45	8.26
6	07-23-07	39°02.778	75°23.776	0.2	25.23	19.5	6.39	7.47	7.18	1.70	10.1
7	07-23-07	39°01.963	75°24.632	0.3	24.88	13.8	4.58	7.11	11.6	5.47	24.1
8	07-23-07	39°00.465	75°26.392	1.1	24.74	2.82	6.03	7.23	3.59	51.3	117.5
9	07-23-07	39°00.725	75°27.066	0.2	23.55	6.8	2.34	6.90	24.2	2.96	13.2
10	07-23-07	39°00.720	75°27.758	0.1	23.50	6.6	5.14	7.61	8.49	0.53	5.28
	Spring 2008 Creek Flux Cores										
5	04-27-08	39°03.039	75°23.427	0.2	15.65	7.29	8.44	7.30	10.24	1.92	52.5
6	04-27-08	39°02.778	75°23.776	0.2	16.82	9.19	8.25	6.98	4.43	0.71	12.9
7	04-27-08	39°01.963	75°24.632	0.3	15.21	2.88	9.64	7.28	6.60	2.33	46.4
8	04-27-08	39°00.465	75°26.392	1.1	16.13	2.71	9.87	7.52	4.41	2.90	53.2
9	04-27-08	39°00.725	75°27.066	0.2	15.26	2.16	8.72	7.66	7.29	2.62	47.1
10	04-27-08	39°00.720	75°27.758	0.1	14.60	1.78	7.88	8.76	6.46	2.56	45.4

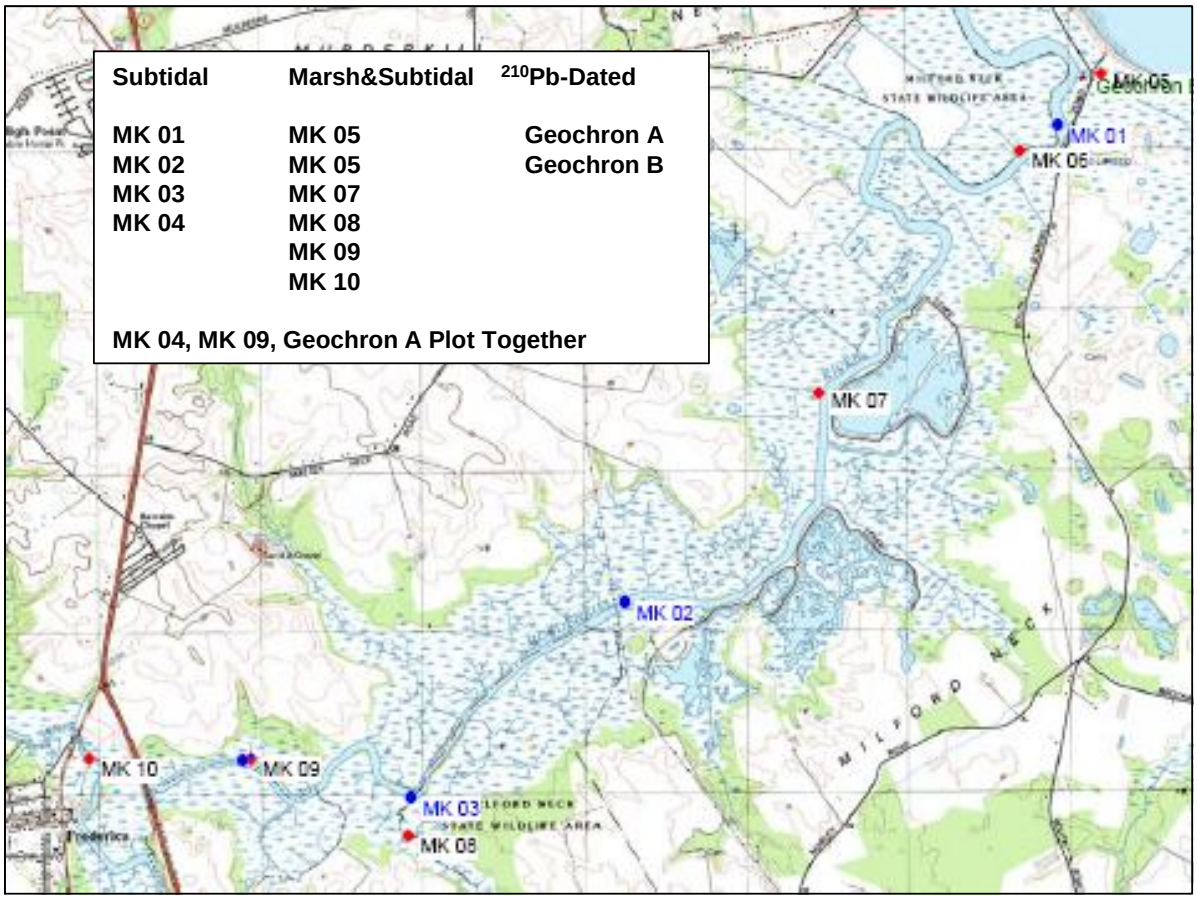


Figure 1. Station locations for Murderkill sediment flux study.

METHODOLOGY

Water Sampling: Water column dissolved oxygen, temperature, salinity, and pH were measured with a YSI model 600R sonde and 650MDS handheld logger. Incubation bottom water was collected at each site using a diaphragm pump; an inline filter removed particulates > 1 μm.

Sediment sampling: Cores for subtidal sediments were collected using a pole corer. The incubation cores consisted of an acrylic tube with an inside diameter of 7 cm and a length of 30 cm overall. This device uses a valve to close the opening above the core, allowing the core to be collected without loss through the bottom and with minimum disturbance of the sediment-water interface. Marsh cores were hand collected by hand insertion into the soil. At each marsh site, we collect a subtidal core from the shallow creek bottom and one core each from each side of the creek. Two marsh cores were collected for sediment chronology/nutrient burial using a Russian peat corer (Figure 2); cores were 60 cm in length.

Incubations: The N_2:Ar denitrification procedure requires flooded cores; cores collected with no overlying water had water added to them. A magnetic stirring system was used to mix the overlying water in each core and the cores were incubated in the dark at *in situ* temperatures (e.g. (Kana et al. 2006). A bottom water blank consisting of a core tube with water only (to compensate for water column metabolism and nutrient cycling) was incubated simultaneously with the sediments.

We bathed the open sediment cores for a period > 12 hours in overlying water from the site; a bubbling system was used to circulate the water and to keep oxygen concentrations near saturation. We measured time courses of dissolved oxygen, di-nitrogen, argon, reactive phosphorus, ammonium, and nitrate.

Water samples were collected by gravity and solute samples were syringe filtered using a 0.45 μm disposable filter unit. Samples for soluble reactive P, ammonium and nitrate were preserved by freezing until chemical analysis. Gas (N_2, O_2, Ar) samples were collected in 7 mL ground-glass stoppered vials and preserved by adding mercuric chloride. They were analyzed by membrane inlet mass spectrometry (Kana et al. 1994). Nutrient analyses were carried out at the Chesapeake Biological Laboratory's Analytical Services group (http://nasl.cbl.umces.edu/).

During the July 2007 sampling, an experiment was carried out to determine the effect of added nitrate on denitrification rates. This experiment utilized the one subtidal and two marsh cores taken from the 6 marsh sites and was designed to examine the quantitative response of marsh and subtidal sediments to added nitrate, as well as determine if the rate of denitrification was nitrate-limited. After the ambient sediment-water exchange experiments were completed, those flux cores had ~ 50 μmol L^{-1} nitrate added to the whole incubation setup. After equilibration overnight, sediment-water exchange of N_2-N was measured. After the 50 addition, another ~50 μmol L^{-1} of nitrate was added and fluxes measured a third time. Nitrate concentrations in each core were measured at the

outset of each experiment.

Sediment-water exchange rates are calculated from the slope of the change of chemical constituent concentrations in the overlying water:

$$F = \frac{\Delta C}{\Delta t} * \frac{V}{A}$$

Where F is the flux (μmol m^{-2} h^{-1}), ΔC/Δt is the slope of the concentration change in overlying water (μmol L^{-1} h^{-1}), V is the volume of the overlying water (L) and A is the area of the incubated core (m^{-2}). When the water-only control core has a significant slope, the slope of the flux cores is adjusted accordingly. Photographs of all 2007 cores after incubation are shown in Figures 3 and 4.

Figure 2. Core collection using a Russian peat corer, July 2007.

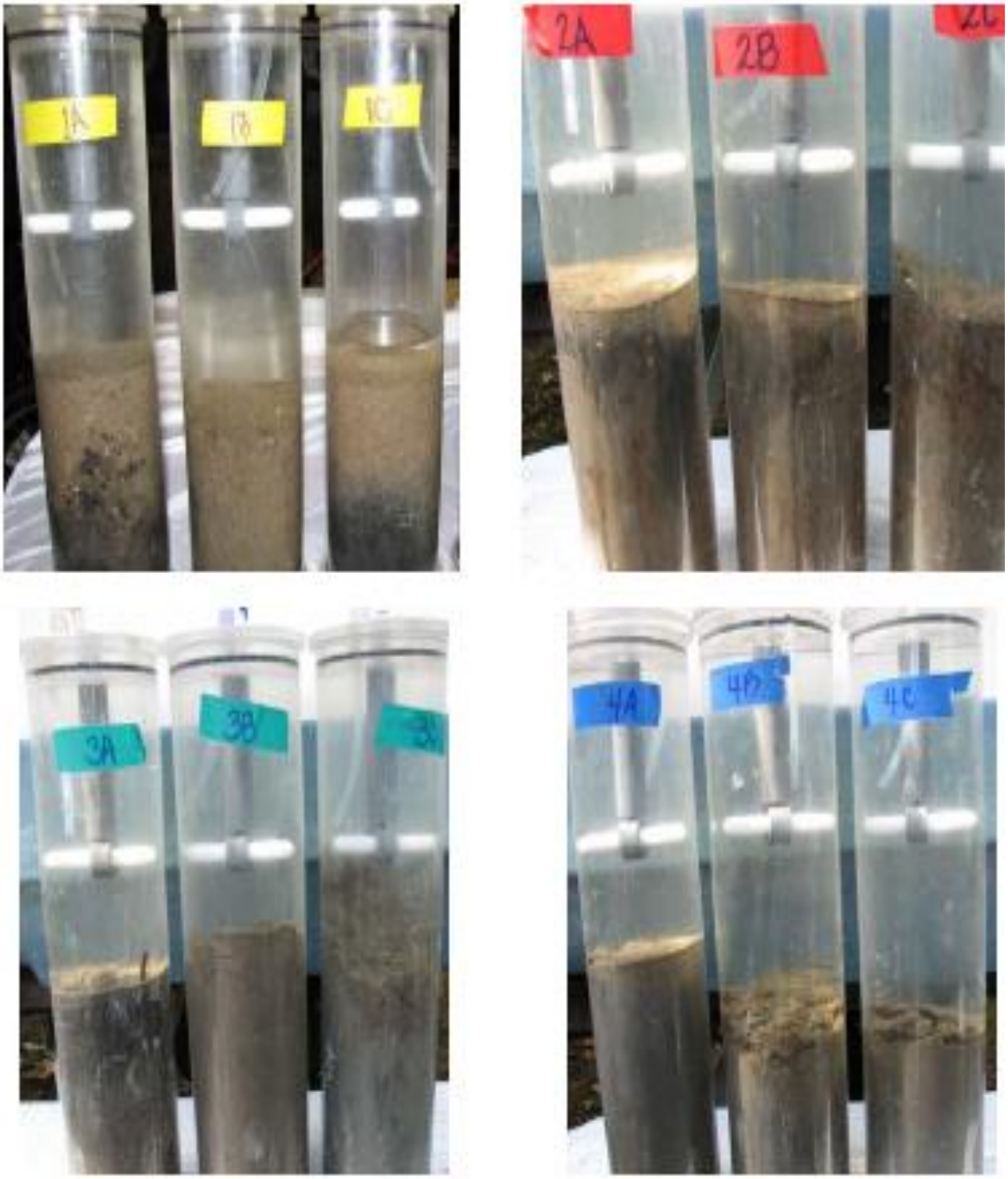


Figure 3. Photos of triplicate subtidal cores from the Murderkill River in July 2007, sites 1-4. Note the coarse grain size several cm below the sediment surface at Site 1, and the surface terrestrial/marsh debris at Site 4.

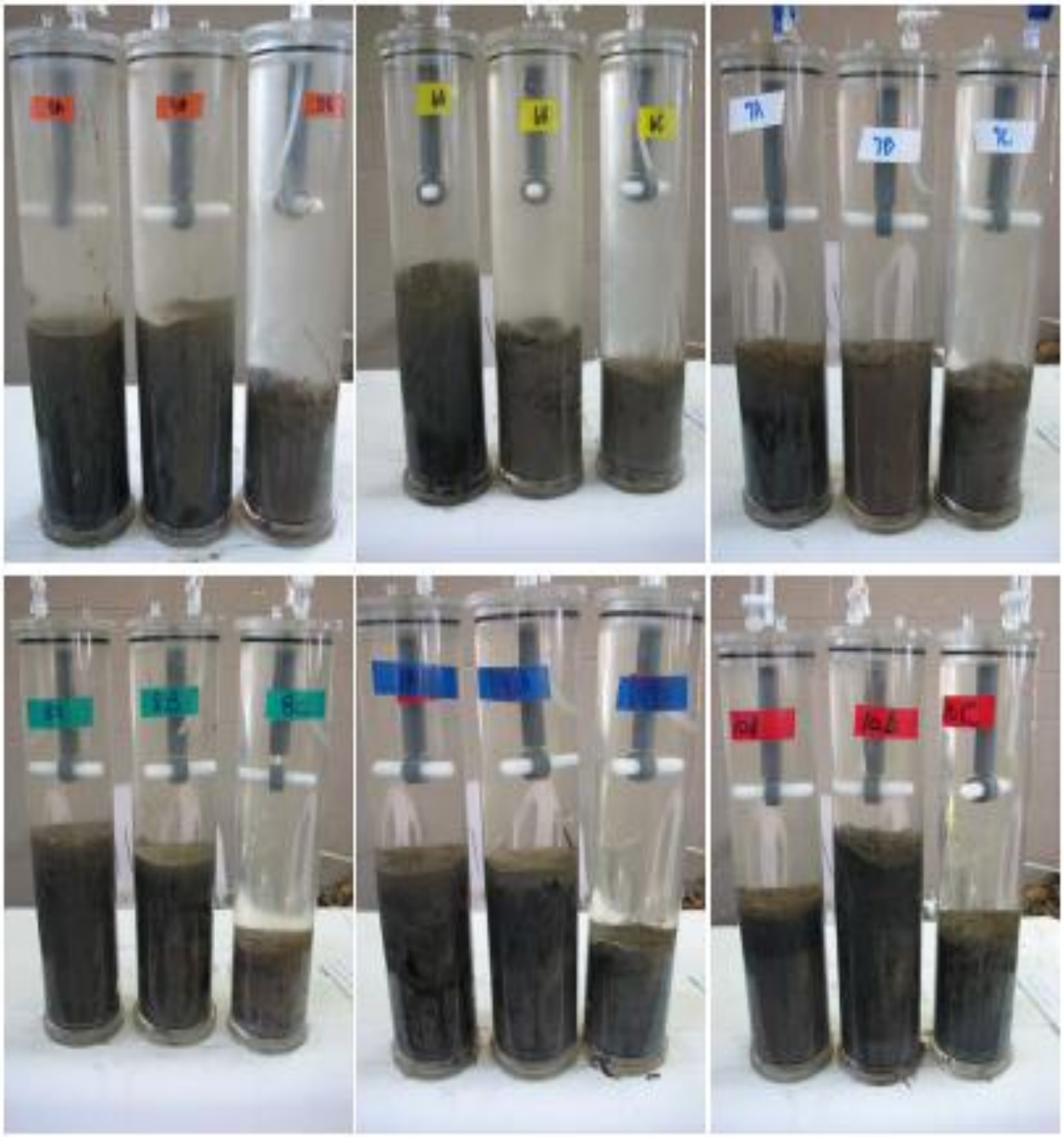


Figure 4. Triplicate cores from the subtidal marsh transect (Sites 5-10), July 2007. In each set, core "A" is a subtidal core and cores "B" and "C" are from the marsh surface.

RESULTS

Creek Chemistry:

The creek water quality data (Table 1) showed temperatures ranging from 23.5-28.0°C in July 2007 and from 14.6-16.8°C in April 2008. Salinity in summer 2007 was much higher than spring 2008, reflecting changes in the freshwater input. In summer 2007, the salinity ranged from 6.6 in the upper river to 20.4 near the mouth; in contrast, the range was 1.8-9.5 in spring 2008. The summer dissolved oxygen data ranged from a near-hypoxic 2.3 mg L^{-1} to 6.2 mg L^{-1} near the Delaware Bay. The pH was generally between 6.5-7.6, with on high value at the freshwater end member in April 2008. This high pH suggest high rates of photosynthesis occur; CO_2 depeletion results in pH elevation. Site 8, receiving treated waste water had the highest nitrate and SRP concentrations in summer, but most spring nitrate values were uniformly high. Some moderate ammonium concentrations were observed, but nitrate was the dominant form of dissolved inorganic N at most sites.

Subtidal Fluxes:

Oxygen**.** Two distinct types of subtidal cores were collected. In July 2007 triplicate cores from the main part of the river were collected, as well as single cores from 6 shallow water marsh creek sites. All average rates for sediment oxygen flux were between -385 and -2,517 μmol m^{-2} h^{-1} (Table 2). The main river sites in July 2007 showed higher O_2 flux rates in the upper river (Figure 5) while the highest marsh creek rates were in the lower river. Site 1, closest to Delaware Bay, was somewhat coarser in grain size than all other sites, with less accumulation of organic matter. These O_2 uptake rates are high, but unexceptional. Core to core variability was somewhat higher than in other systems we have studied but on a par with other Delaware Bay tidal rivers (Owens and Cornwell 2002); heterogeneity in surficial deposits was evident from a visual inspection of the cores. The July 2007 data for tidal creek-river adjacent sites shows excellent correspondence between nearby sites 3 and 8 and poor correspondence between sites 1 and 6.

Ammonium**.** Summer **a**mmonium fluxes were high in two main stem subtidal cores (3 and 4) and four of six shallow water subtidal cores (Figure 6); all winter rates were low. Very low rates were observed at stations 1, 2 and 7 in summer 2007. The high July 2007 rate at station 10 is entirely inconsistent with the apparent low oxygen flux and suggests that the ammonium flux is not simply a function of decomposition within surface sediment horizons, but perhaps reflects groundwater inputs of ammonium.

Nitrate**.** The fluxes of nitrate plus nitrite were variable and generally low at the river sites, with highest rates observed at stations 7-9, though the rates changed from season to season (Figure 7). The highest rates of nitrate flux were directed into the sediments at rates of 100-300 μmol m^{-2} h^{-1}. The influx of nitrate can have multiple fates, supporting both denitrification and DNRA. DNRA is the dissimilatory nitrate reduction to

ammonium, and often is found in reducing estuarine sediments (Koop-Jakobsen and Giblin 2010); put simply nitrate is converted to ammonium.

Denitrification. The term denitrification is used interchangeably with N_2-N efflux throughout this report; the discovery of the anammox process in nature has provided another NO_{2+3}^- reduction pathway, one in which ammonium and nitrite react to form N_2. This pathway has generally been found to be of negligible impact in shallow subtidal sediments (Rich et al. 2008) and tidal marshes (Koop-Jakobsen and Giblin 2009). Denitrification rates were measurable and generally high at all sites. The highest rates in the main stem subtidal cores approached 400 μmol m^{-1} h^{-1} (Figure 8), rates that are among the very highest observed in coastal ecosystems. In July 2007, rates range from <30 to > 350 μmol m^{-2} h^{-1}, with the highest rates at sites 3, 7, 8 and 9, all in the middle to upper river. During April 2008, nitrate concentrations were higher at 5 of 6 sites that observed in summer; spring rates were higher in half of the observations. The pattern in rates are not easily identified, but they are in fact consistent with a combination of denitrification driven by water column nitrate (see nitrate uptake rates) and coupled nitrification-denitrification (i.e. Cornwell et al. 1999). In cases where low or negligible nitrate uptake is found, denitrification is supported by nitrification occurring within the sediments. Such nitrification requires oxygen within surficial sediments, while denitrification occurs where oxygen is depleted.

SRP Fluxes**.** The fluxes of SRP from sediment was generally very low (Figure 9, Table 2), with the highest efflux rates in the lower estuary shallow water sites. There were 6 site occupations with next SRP efflux, 5 with net SRP influx, and the remainder with insignificant flux. No discernable seasonal or spatial pattern was evident, and sites with high ammonium efflux did not necessarily have high SRP efflux, indicating divergent biogeochemical pathways. It would appear that SRP recycling is not a key process in this system.

Regional Comparison. The rates of sediment oxygen demand observed in subtidal sediments of the Murderkill River and shallow-water creeks were generally within the range observed for other east coast estuaries, including Delaware Bay (Table 3). Summer oxygen fluxes tended toward the lower end of the regional data set, but Murderkill ammonium, nitrate and SRP fluxes appeared similar to many other ecosystems. Denitrification rates in this study appear higher than other Delaware Bay marsh rivers and shallow water bays.

Table 2. Fluxes for individual subtidal cores. ns indicates non-significant fluxes.

.

Subtidal	O_2	N_2-N	NH_4^+	SRP	NO_2^-+NO_3^-
	μmol m^{-2} h^{-1}				
	Main River Subtidal July 2007				
1a	-685.9	106.6	-5.8	-4.0	-24.0
1b	-398.6	60.7	133.1	10.7	-30.2
1c	-70.1	35.8	-14.6	0.8	-26.2
2a	-776.9	110.3	-37.4	0.0	0.0
2b	-827.8	146.1	-14.6	0.0	-79.3
2c	-1752.2	256.3	58.6	-8.2	-95.4
3a	-921.1	133.3	ns	62.2	-109.7
3b	-2342.4	442.0	558.9	-23.4	-214.2
3c	-1405.1	643.4	508.0	-0.3	-392.2
4a	-1336.0	250.6	158.4	-21.6	-55.3
4b	-1475.5	173.3	204.5	4.4	-89.4
4c	-1285.5	141.5	206.7	-25.1	-58.2
	Creek Subtidal – July 2007				
5a	-2517.0	107.2	531.4	22.2	-49.2
6a	-1924.1	26.8	243.8	5.6	-14.0
7a	-276.7	109.8	2.4	3.7	-146.9
8a	-1344.9	207.4	60.4	0.0	-246.7
9a	-1040.0	ns	276.0	ns	0.0
10a	-237.6	70.2	632.2	-29.4	0.0
	Creek Subtidal – April 2008				
5a	-956.2	74.3	0.0	-5.6	0.0
6a	-938.9	69.3	45.2	11.4	39.5
7a	-2134.9	369.6	85.1	-18.7	-301.4
8a	-2049.2	156.2	56.9	0.0	Ns
9a	-1229.5	180.6	26.5	-5.8	-197.0
10a	-869.1	77.4	ns	ns	ns

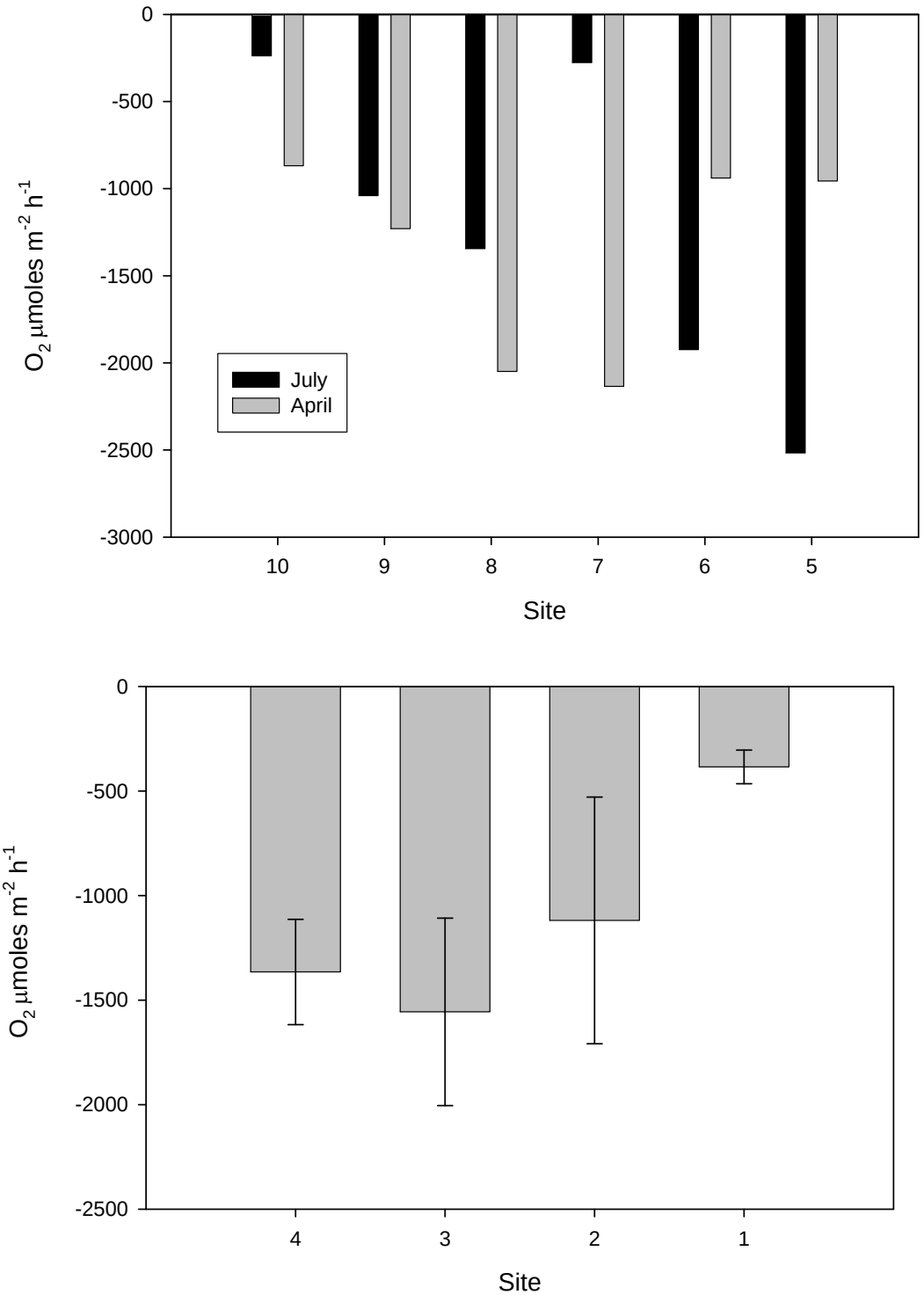


Figure 5. Subtidal sediment oxygen demand in July 2007 and April 2008; negative values indicate flux into the sediment. The error bars on the lower panel are standard deviation (N = 3) for river cores, the upper panel creek sites sampled in July 2007 and April 2008 were not replicated.

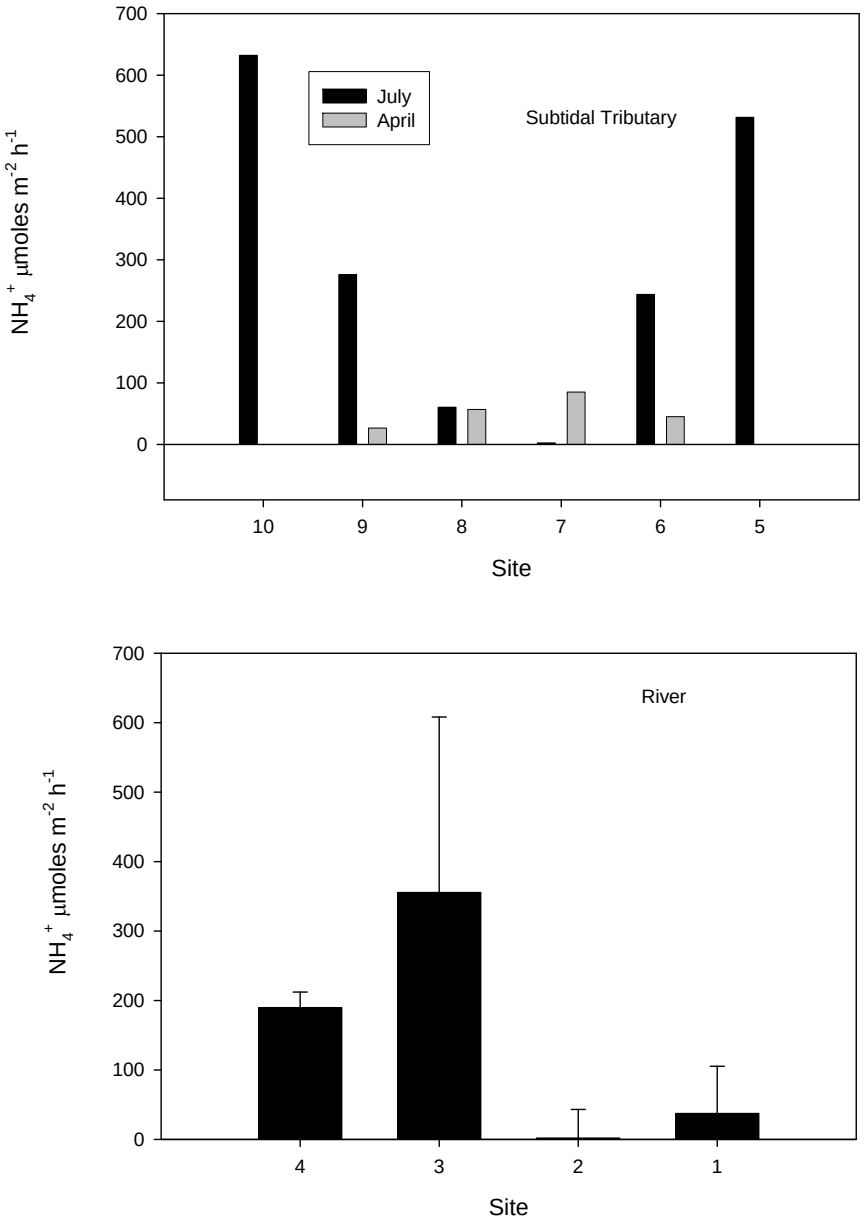


Figure 6. Subtidal sediment ammonium fluxes in July 2007 and April 2008. The error bars on the lower panel are standard deviation (N = 3) for river cores, the upper panel creek sites sampled in July 2007 and April 2008 were not replicated.

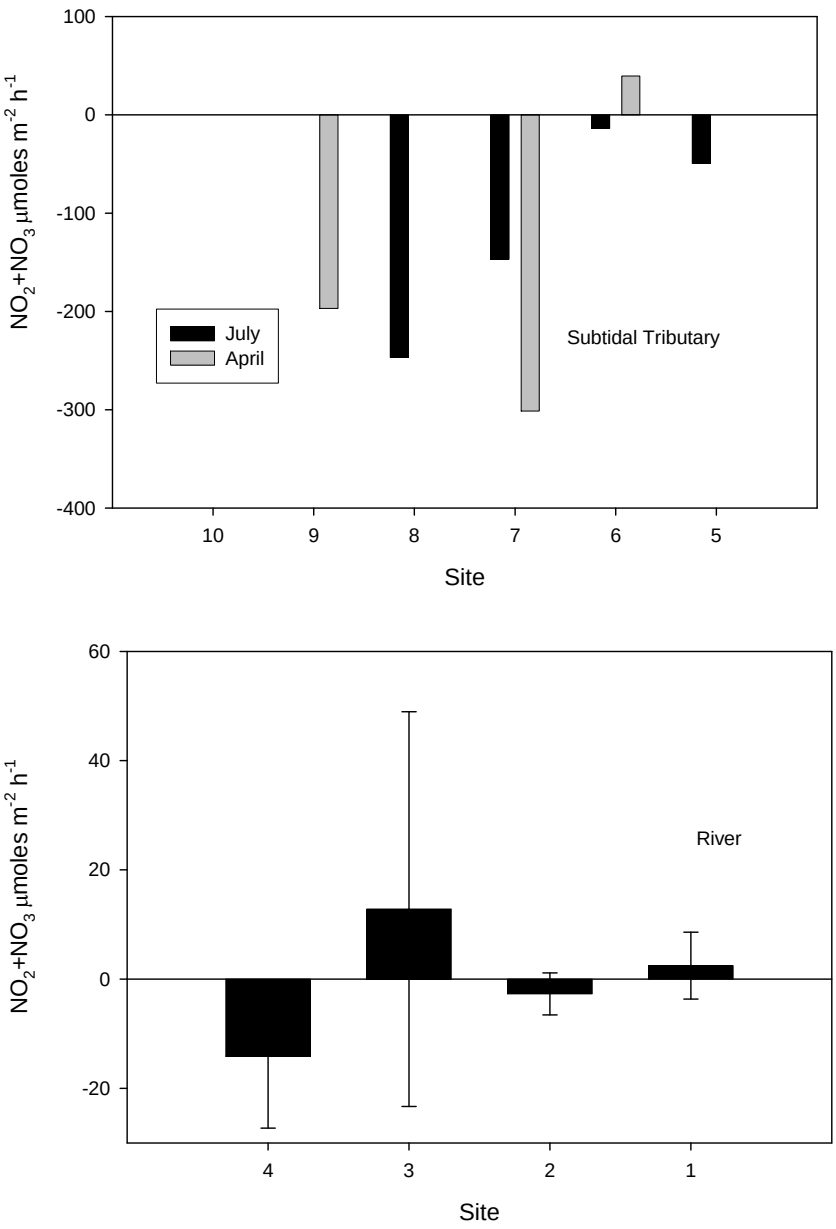


Figure 7. Subtidal nitrate flux rates in July 2007 and April 2008; negative values indicate flux into the sediment. The error bars on the lower panel are standard deviation (N = 3) for river cores, the upper panel creek sites sampled in July 2007 and April 2008 were not replicated.

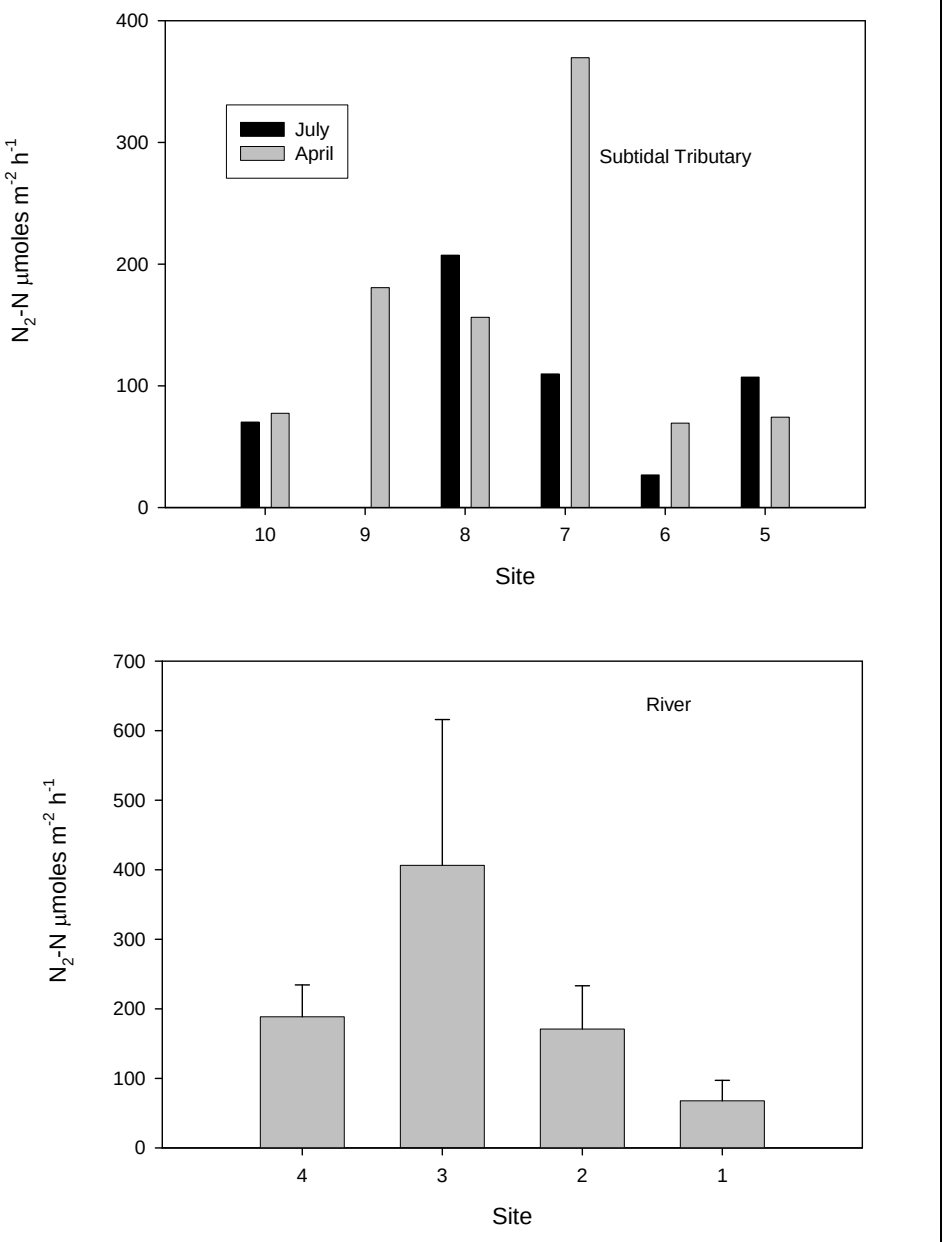


Figure 8. Subtidal N_2-N flux rates in July 2007 and April 2008. The error bars on the lower panel are standard deviation (N = 3) for river cores, the upper panel creek sites sampled in July 2007 and April 2008 were not replicated.

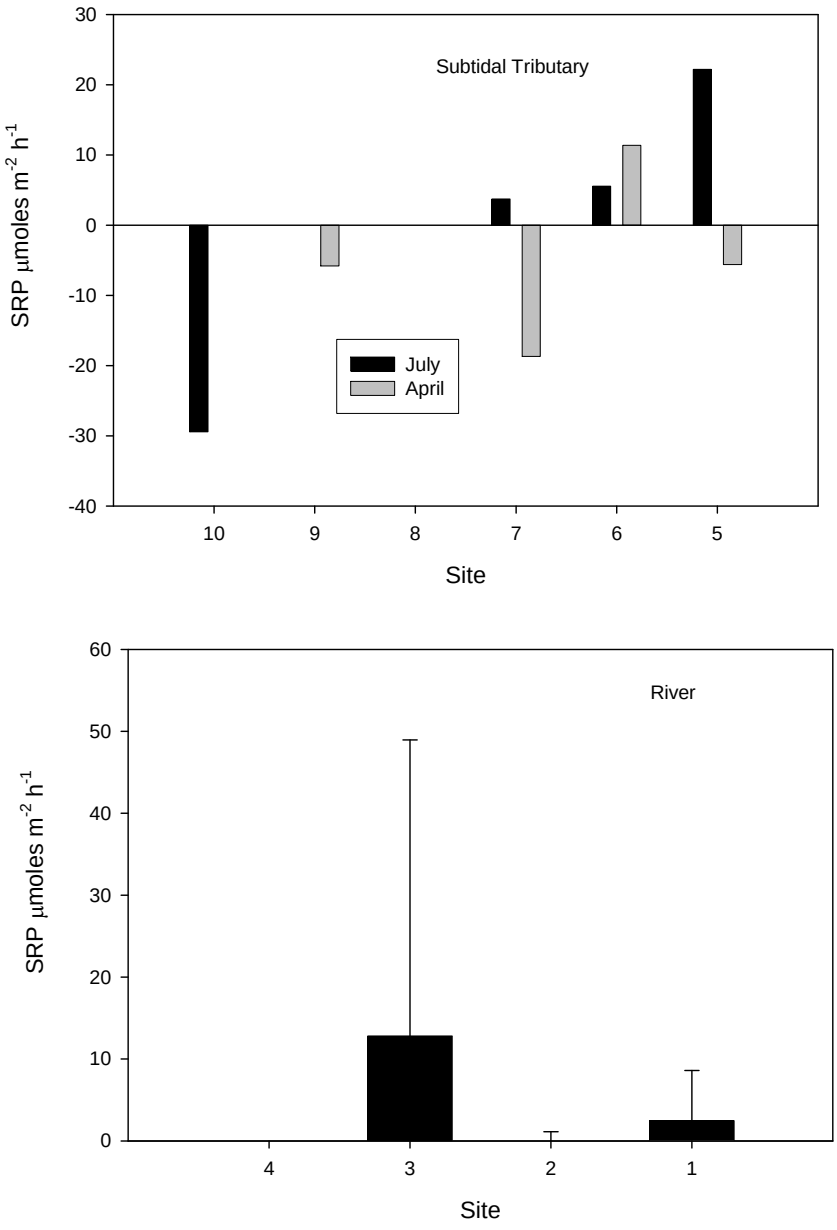


Figure 9. Subtidal SRP flux rates in July 2007 and April 2008; negative values indicate flux into the sediment. The error bars on the lower panel are standard deviation (N = 3) for river cores, the upper panel creek sites sampled in July 2007 and April 2008 were not replicated.

Table 3. Comparison of subtidal nutrient flux rates in shallow water US east coast environments.

	Sediment-Water Exchange Comparison (μmol m^{-2} h^{-1})					
System	Oxygen Uptake	N_2-N	NH_4^+	NO_3^-	PO_4^{3-}	Reference
Delaware River	853 to 2947	No Data	0-1078	-512 to –28	-3 to 20	(Owens and Cornwell 1997)
Delaware Bay	1734	No Data	68	74	No Data	(Seitzinger 1988)
LI Bays – Aug Sand	521-1196	No Data	-22-107	-13-5	-4 to -1	(Howes et al. 1998)
LI Bays Aug Mud	1546-4492	No Data	8-764	3-59	-3 to 74	
LI Bays April Sand	1275-2050	No Data	-6 to -5	-14-0	0 to 1	
LI Bays April Mud	954-2679	No Data	-7-29	-12-13	-1 to 4	
Shallow Chesapeake (Summer Silt/Clay)	3844		580	4	33	(Reay et al. 1995)
Indian River-Rehoboth Bay Dark	600-3700	No Data	100-450	0-15	0 to 14	(Cerco and Seitzinger 1997)
Indian River	1095-2685	12-125	54-368	-113-16	0	(Owens and Cornwell 2002)
Buoy 6	1071-5429	0	0-439	0	0	
DC	739-2306	0-113	0 -189	-55-26	-5.1 to 10.5	
St. Jones I	1315-2570	27-166	-3-39	-28--24	-17-14	(Owens and Cornwell 2003)
St. Jones II	1145-1246	0-76	17-570	-32-2	-2-59	
Broadkill I	859-2100	113-217	223-1212	-510 - -81	-5-10	
Broadkill II	778-1011	28-68	71-405	-102 - -4	-0.2-32	
Murderkill 1	385±80	68±29	38±68	-27±3	2±6	This Study
Murderkill 2	1119±590	171±62	24±1	-58±42	-3±4	
Murderkill 3	1556±449	406±210	356±252	-239±116	13±36	
Murderkill 4	1366±252	188±46	190±22	-68±15	-14±13	

Marsh Fluxes

Oxygen. Oxygen uptake rates on an individual core basis ranged from -450 to -2,100 μmol m^{-2} h^{-1} (Table 4) with rates generally similar to subtidal sediments. The highest oxygen uptake rates on each sampling date were in the upper river (Figure 10); replicate cores taken from opposite sides of the marsh creek were in reasonable agreement (Table 4). The oxygen uptake data from the Murderkill marsh complex are generally smaller than those determined by (Greene 2005) in the upper Patuxent River (mean = -2109, median = -1757 μmol m^{-2} h^{-1}). Greene's data showed higher rates during mid-summer while the Murderkill had higher rates in the spring.

Denitrification. Denitrification rates were uniformly high in the marsh cores (Figure 11), with all rates in excess of 70 μmol m^{-2} h^{-1} (Table 4). Although the highest subtidal rates exceeded the marsh rates, the large surface area of the marsh would suggest that the marsh surface is a key place for denitrification in the Murderkill system. Seasonality in the rate of denitrification is not indicated in this data set. It is clear that both marsh and subtidal sediments are important for denitrification. Several studies have used comparable techniques for denitrification in tidal wetlands. Greene's (2005) tidal fresh/oligohaline Patuxent data showed an overall average denitrification of ~120 μmol m^{-2} h^{-1} N_2-N flux, while (Hopfensperger et al. 2009) tidal fresh Potomac River marsh data showed an average of 147±24 μmol m^{-2} h^{-1} N_2-N flux. Those rates are virtually identical to those in this study.

Ammonium. Ammonium effluxes were variable with higher rates in the upper and lower estuary (Figure 11), with July 2007 data closely mirroring the pattern observed for subtidal sediments. The rates were quite variable, with a number of April 2008 rates directed into the sediment. Overall these data are consistent with data from the Patuxent River tidal marshes (Greene 2005).

Nitrate. In July 2007 nitrate + nitrite fluxes were directed into the sediments at two sites (8 and 10), and out of the sediments at 5 and 7. The largest nitrate uptake was > twice the denitrification rate for the corresponding cores. In April 2008, 4 of 6 sites had large nitrate + nitrite fluxes directed into the sediments, with one flux out. April nitrate + nitrite influxes at 4 sites were of a similar magnitude as denitrification effluxes.

SRP. In July 2007, SRP fluxes were directed into the sediment at two sites (7 and 8), with modest outward effluxes at 6 and 9. In April 2008, all SRP fluxes were relatively low, with some directed into sediments and others directed out of sediment.
Subtle differences in iron and sulfur biogeochemistry are likely the cause of these differences (Chambers and Odum 1990; Roden and Edmonds 1997).

Table 4. Marsh flux rates. ns indicates an uninterpretable flux time course.

Marsh	O_2	N_2-N	NH_4^+	SRP	NO_2^-+NO_3^-
	μmol m^{-2} h^{-1}				
	July 2007				
5b	-448.0	56.5	27.5	0.0	32.4
5c	-901.9	183.6	67.7	0.0	0.0
6b	-1035.0	116.3	ns	23.5	0.0
6c	-1256.9	130.5	126.6	8.1	0.0
7b	-556.9	143.6	23.7	-6.8	1.1
7c	-978.3	209.8	-6.0	-93.2	25.5
8b	-960.1	112.5	23.8	-129.6	-241.4
8c	-1096.0	230.4	17.0	ns	-582.7
9b	-894.1	58.3	130.4	17.7	0.0
9c	-913.9	168.5	75.0	-10.8	0.0
10b	-1962.8	85.9	85.7	0.0	-173.5
10c	-852.6	218.2	228.7	0.0	-103.3
	April 2008				
5b	-1302.3	170.8	-53.7	-5.9	0.0
5c	-1175.0	179.5	-41.3	-7.3	0.0
6b	-1140.7	82.7	10.6	23.0	0.0
6c	-1106.2	78.6	-15.6	-4.6	0.0
7b	-1036.2	199.2	-82.5	0.0	790.6
7c	-1020.8	282.1	0.0	0.0	ns
8b	-1309.2	72.7	-50.4	-19.7	-133.0
8c	-1161.2	109.2	8.5	0.0	-377.1
9b	-1733.4	187.8	-9.0	-1.6	ns
9c	-1085.1	102.3	34.7	-5.9	0.0
10b	-1667.4	158.3	-42.8	-17.9	ns
10c	-2011.2	95.2	39.3	-10.7	-747.9

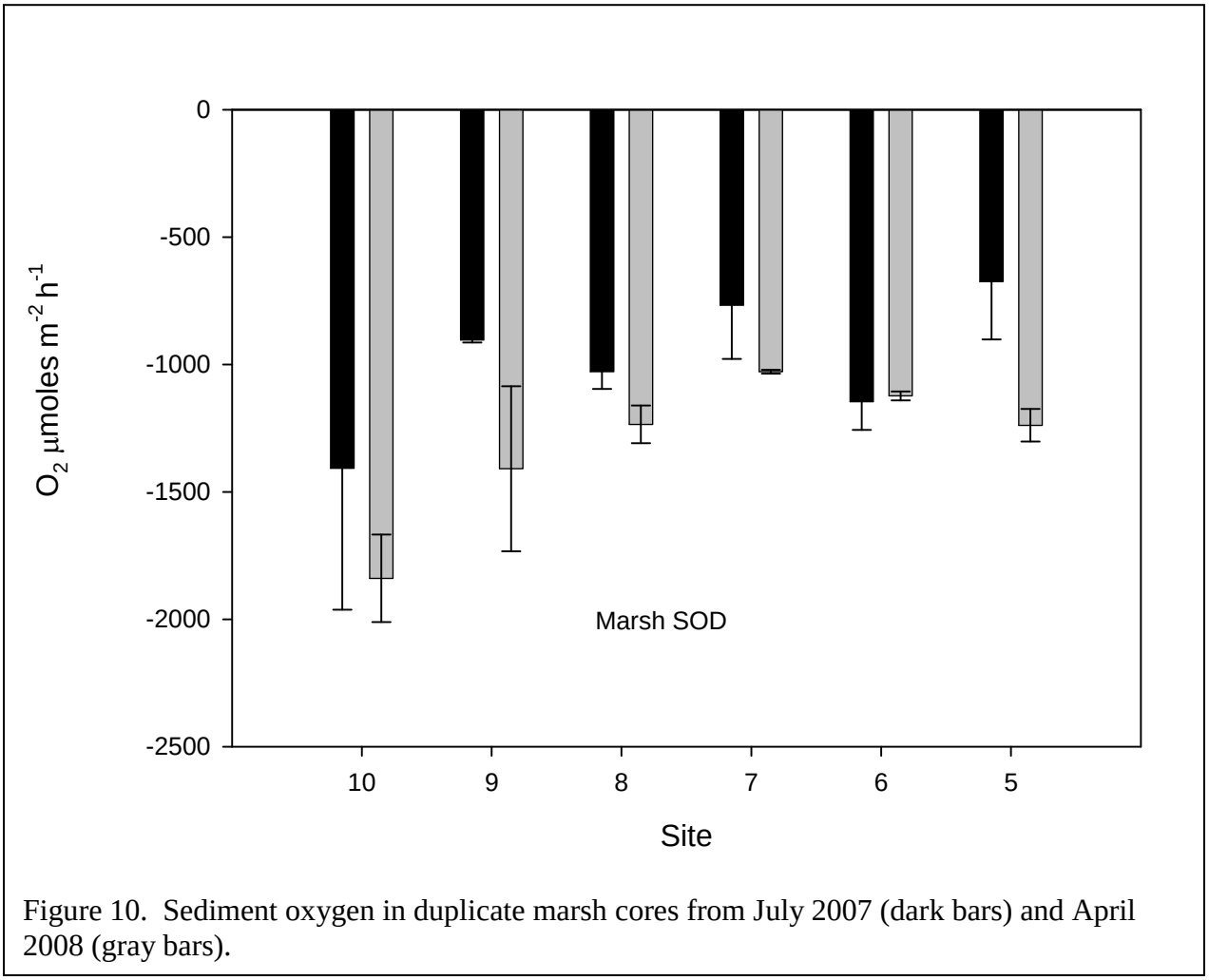
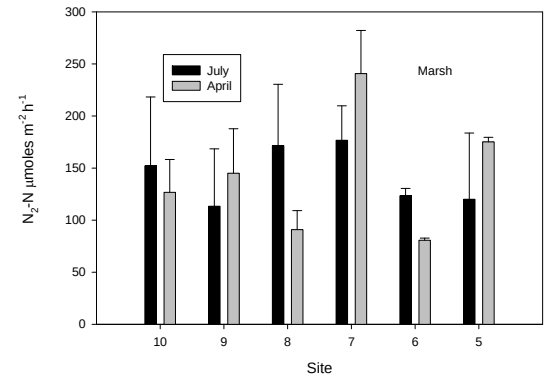


Figure 10. Sediment oxygen in duplicate marsh cores from July 2007 (dark bars) and April 2008 (gray bars).



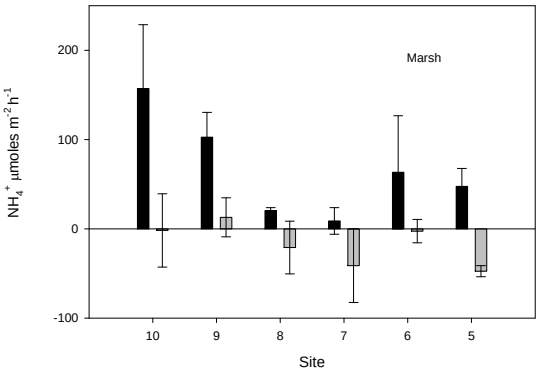
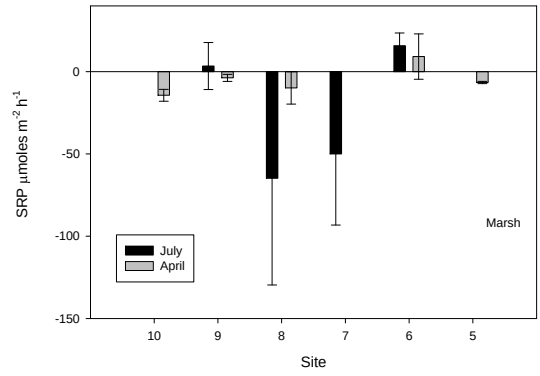


Figure 11. N_2-N fluxes (upper panel) and ammonium fluxes (lower panel) from duplicate marsh cores.



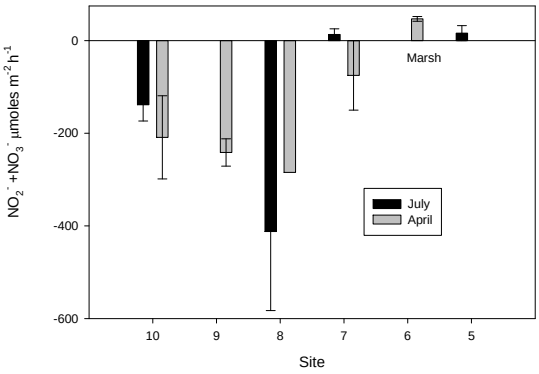


Figure 12. SRP fluxes (upper panel) and nitrate+nitrite fluxes in duplicate marsh cores.

Marsh Fluxes: Effects of Added Nitrate

The nitrate concentration in the nitrate addition experiment was strongly affected by the original nitrate in the overlying water. In particular, the high nitrate at site 8 resulted in very high nitrate + nitrite concentrations in all three treatment levels (Table 5). All data (all marsh and subtidal, ambient and enhanced) are averaged in Figure 13, showing higher denitrification rates generally occur where concentrations of nitrate are higher. The plots of each core with added nitrate are shown in Figure 14. We are pleased with these experimental results, the nitrate response is large even in a short experiment.

Greene (2005) carried out identical experiments on Patuxent River marshes. Her average rate of denitrification with 100 μmol L^{-1} nitrate was slightly greater than 200 μmol m^{-2} h^{-1}, very similar to this study's average rates. The uptake of nitrate includes two key components: 1) diffusion of nitrate to the zone of denitrification and 2) the bacterial response to higher nitrate. With increased rates of sediment oxygen demand, the depth of oxygen penetration decreases (DiToro 2001), and the diffusive distance for added nitrate decreases, thus increasing nitrate uptake. One might expect a strong relationship between rates of denitrification and sediment oxygen demand, but given overall variability, no statistical relationship was evident (Figure 15). At a single site (8) we see a suggestion of a linear relationship.

Table 5. Denitrification rates and nitrate + nitrite concentrations in nitrate addition experiment. Amb indicates ambient (field) nitrate + nitrite concentrations.

Site		N_2-N Flux				$NO_2^-+NO_3^-$		
		μmol m^{-2} h^{-1}				μmol L^{-1}		
		amb	low	high		amb	low	high
5	A	107	212	396		7.79	61.0	122.6
	B	56	148	184		8.35	64.2	118.7
	C	184	362	356		8.16	79.1	122.5
6	A	27	171	192		9.41	62.1	126.7
	B	116	108	157		10.1	61.3	126.1
	C	130	164	144		8.85	65.9	129.3
7	A	110	172	149		23.6	87.1	129.2
	B	144	113	188		23.9	86.0	134.2
	C	210	165	186		23.3	86.8	134.6
8	A	207	300	297		117.7	160.2	215.9
	B	113	189	214		119.1	140.8	217.5
	C	230	318	266		119.3	161.2	225.2
9	A	0	208	191		12.3	66.0	118.2
	B	58	145	173		12.8	72.7	124.3
	C	168	225	211		13.5	67.9	119.2
10	A	70	144	245		5.00	60.9	110.5
	B	86	307	465		5.03	59.5	102.4
	C	218	354	340		4.59	60.5	101.9

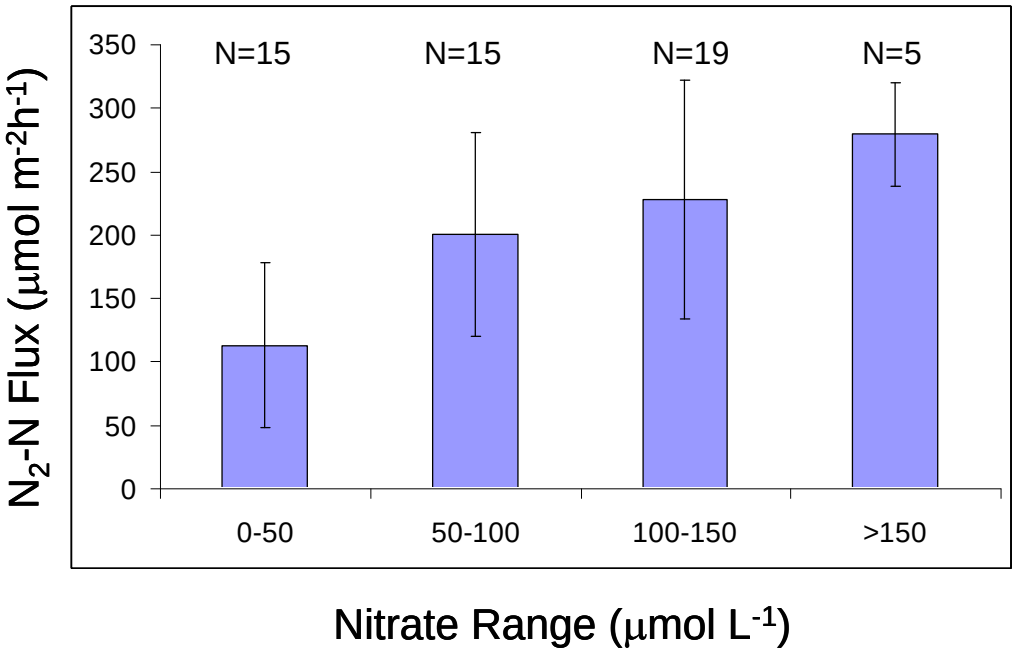


Figure 13. Denitrification rates from multiple cores within a nitrate concentration range. A total of 54 data points are included and both marsh and subtidal cores are included.

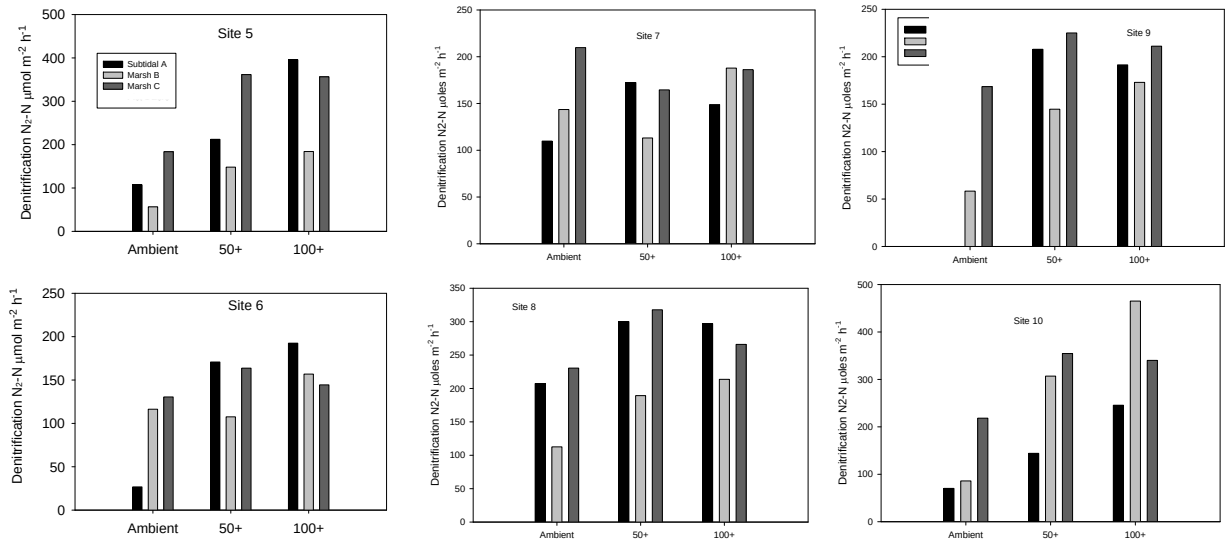


Figure 14. Plots of individual core denitrification rates for 3 concentrations of added nitrate.

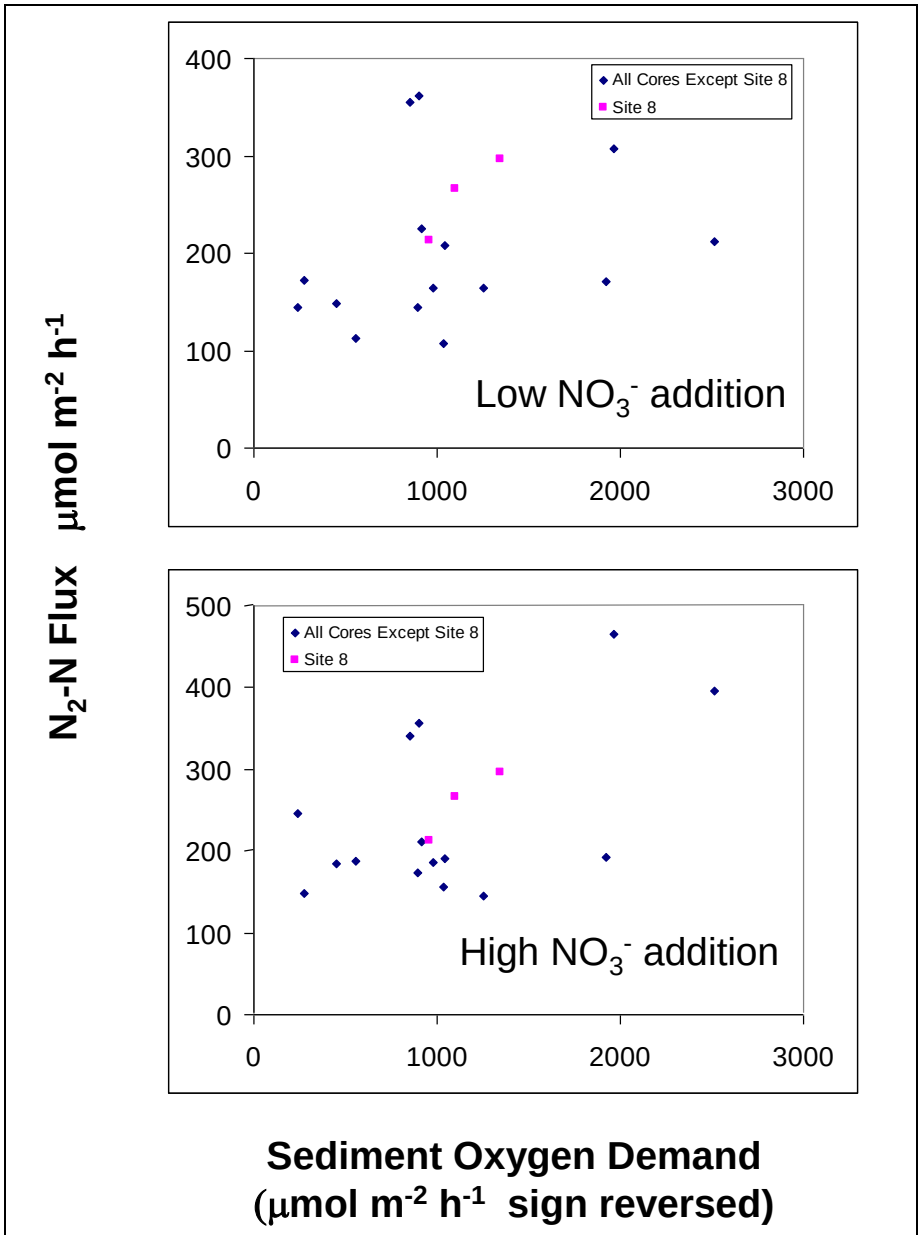


Figure 15. Denitrification rates with added nitrate, plotted as a function of sediment oxygen demand. The lower nitrate addition (upper panel) had a nitrate concentration range of 66-87 µmol L^{-1}, with Site 8 having 141-162 µmol L^{-1}. The higher nitrate addition was 102-134 µmol L^{-1}, with Site 8 having 216-225 µmol L^{-1}. There was no statistically significant relationship.

SOLID PHASE ANALYSES – SURFICIAL SEDIMENTS

Grain Size. Grain size analysis was carried out on each individual core used for sediment-water exchange and denitrification measurements (Figure 16); core depths for this analysis were 10 cm. The river subtidal sediment-water exchange site closest to the Delaware Bay (Site 1) was the only incubated sample in this study that was predominantly sand, with the 3 replicate cores showing the same grain size. Upstream samples were dominantly silt and clay, with a modest amount of sand at Site 2. The July 2007 marsh surface data indicated some variability in grain size, with sand averaging 15±13%. There did not appear to be a systematic difference between subtidal ("A") cores and marsh cores from the same site ("B" and "C" cores). In April 2008, subtidal and marsh cores all appeared to have even less sand. The reason for this difference is not obvious. Regardless, the marsh sites and the shallow subtidal sites are predominantly fine-grained.

Surficial sediment carbon ranged from <0.1 to > 12.5% (Figure 17). The average subtidal river C was 3.0±2.8%; without coarse-grained Site 1, the average increased to 4.3±25%. The combined marsh/shallow creek data sets averaged 7.4±2.2 and 6.6±2.3 for July 2007 and April 2008 sample collections. It is clear that the surficial sediment is primarily inorganic sediment; the concentrations of organic carbon are not particularly high. Nitrogen showed the same patter as carbon (Figure 18), with average river N concentrations of 0.22±0.19% and the July 2007 and April 2008 marsh/marsh creek data each averaging 0.61±0.14 and 0.54±0.18% N respectfully. Organic carbon was ~40% of the value of loss on ignition (Figure 19), with subtidal, July 2007 and April 2008 loss on ignition values of 8.5±7.4, 19.4±3.9, and 18.2±5.1%. For all surficial data, the molar C:N ratio was 14.5 (Figure 19). This value is much higher than that of algae but lower than other surficial core data which ranged from 18.5-30.4 (Velinsky et al. 2010), excepting their core MK-4 which had data which overlapped with these data. The surficial concentrations of N in the Velinsky data set ranged from 0.54 to 1.28% N averaging 0.8%, slightly higher than our marsh surficial data (0.57±0.16%).

Our total P data averaged 0.5±0.5, 1.4±0.3 and 0.9±0.3 mg g^{-1} for river, July marsh and April marsh sampling respectively, with inorganic P averaging 0.3±0.4, 0.8±0.2 and 0.6±0.3 mg g^{-1} for the same samples (Figure 20). Differences between the July and April dates for total P are relatively large and may reflect seasonal differences in the near-surface material. Higher concentrations in July may reflect increased summer post-depositional mobilization of SRP, with desorption at depth and resorption on Fe-oxides near the surface (Chambers and Odum 1990; Bryner 2000).

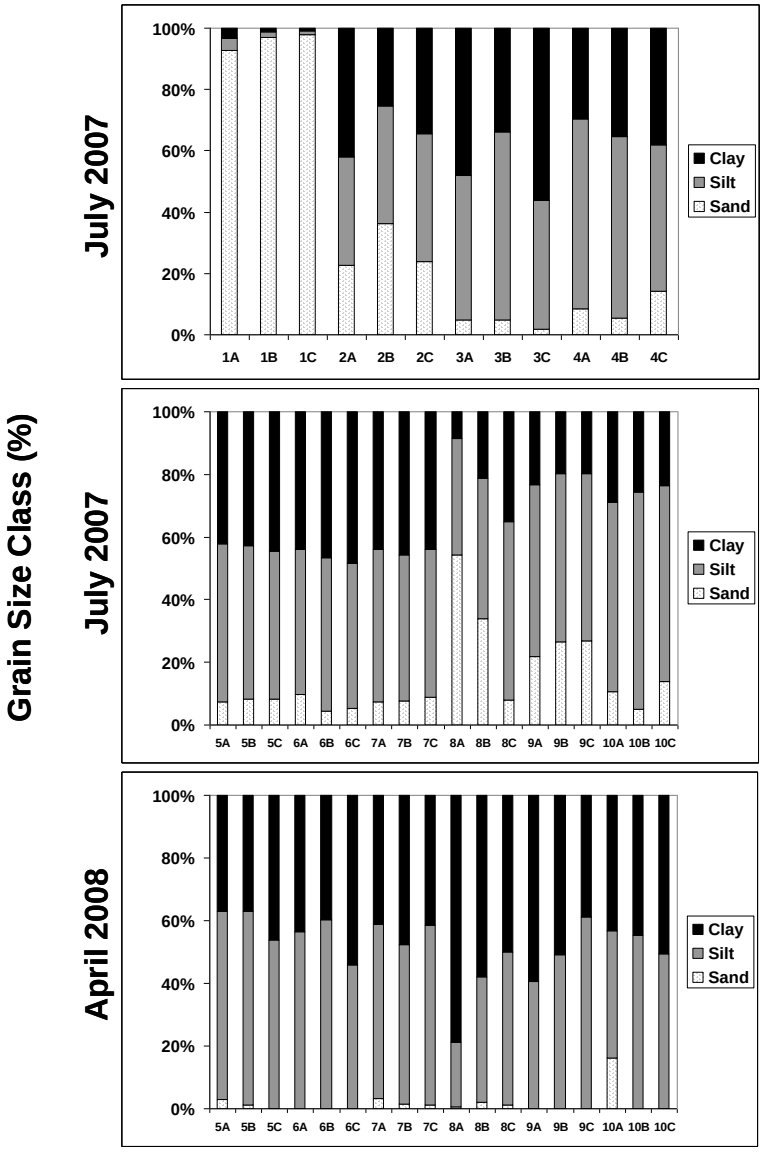


Figure 16. Grain size.

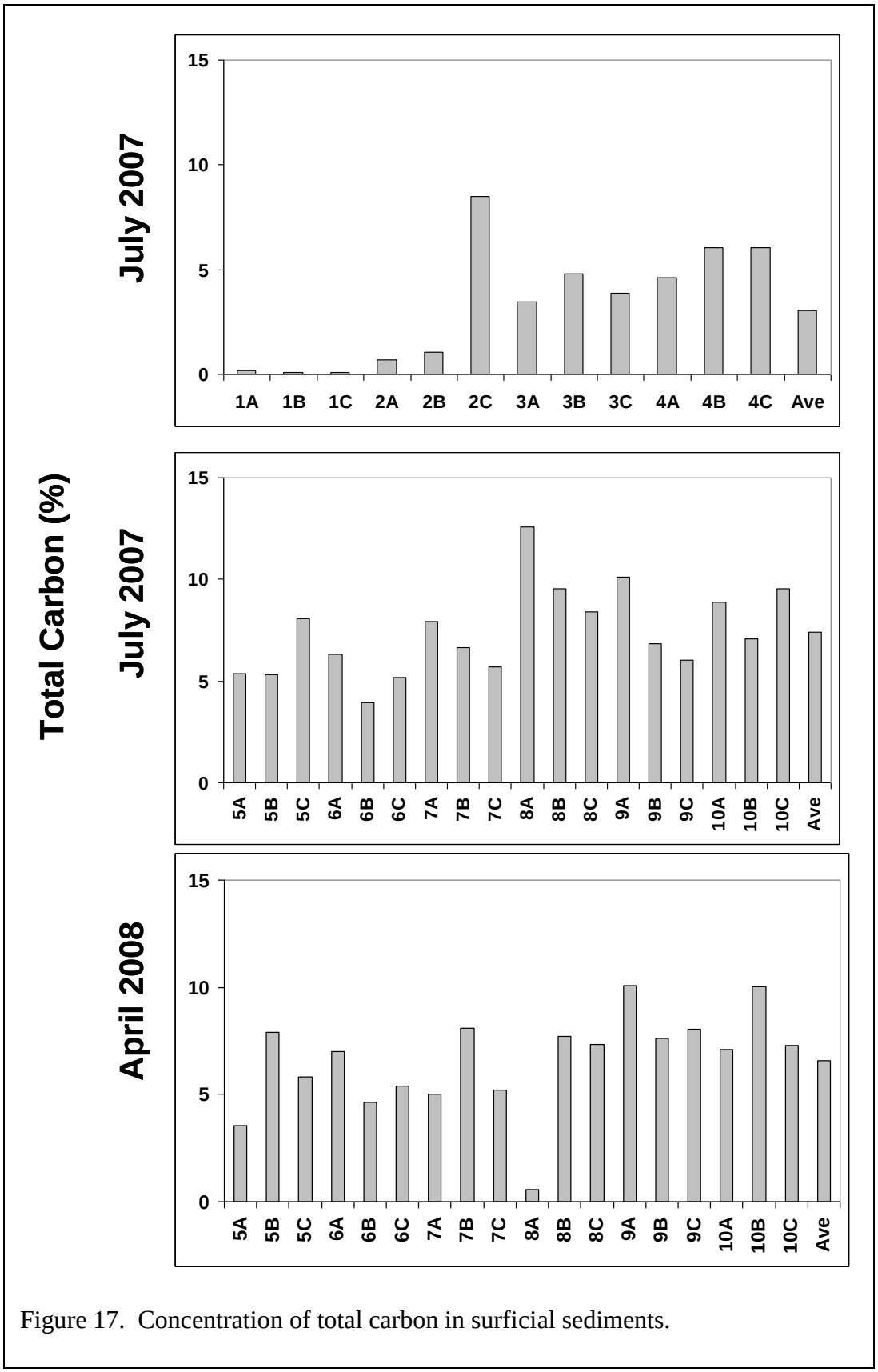


Figure 17. Concentration of total carbon in surficial sediments.

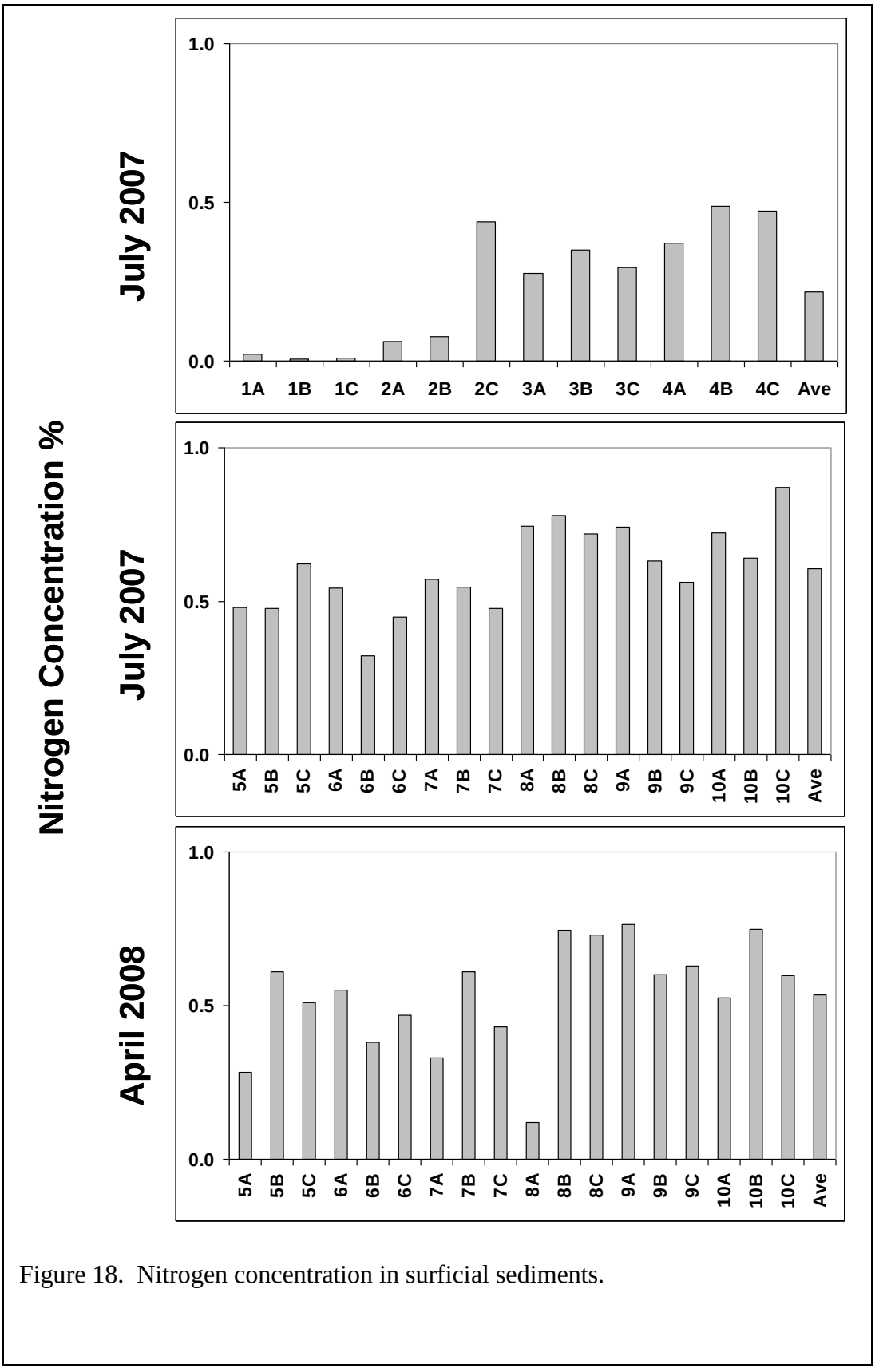


Figure 18. Nitrogen concentration in surficial sediments.

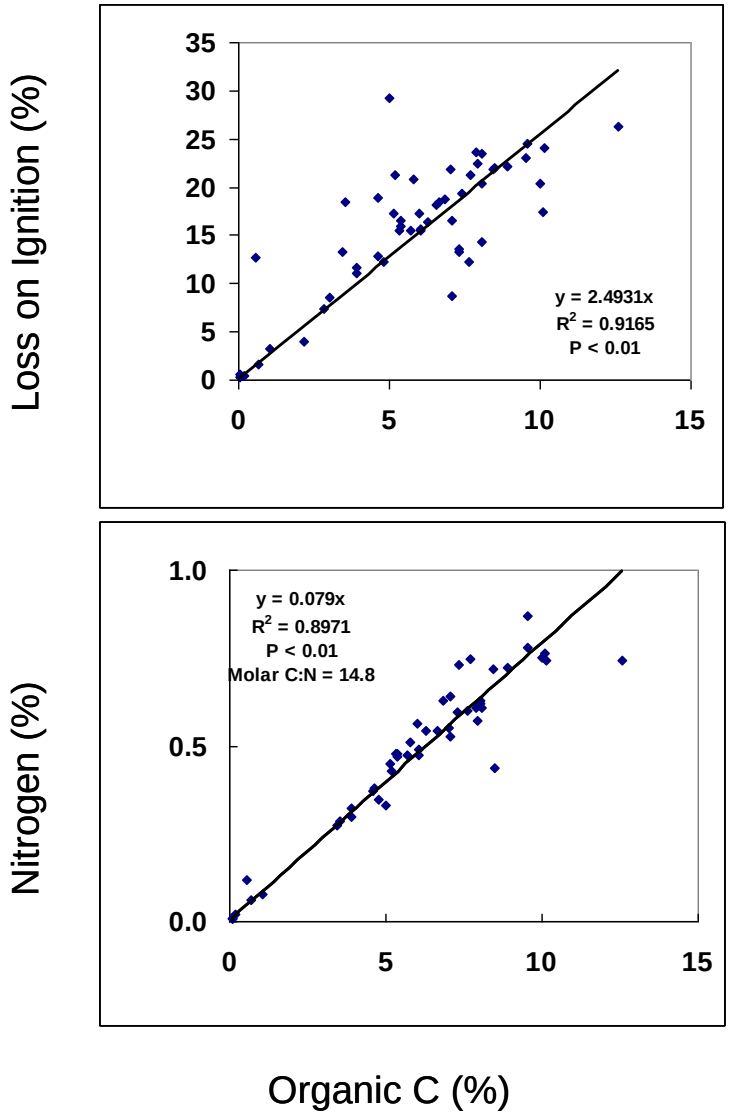


Figure 19. Surficial sediment organic carbon versus nitrogen and loss on ignition. All marsh and subtidal samples are included.

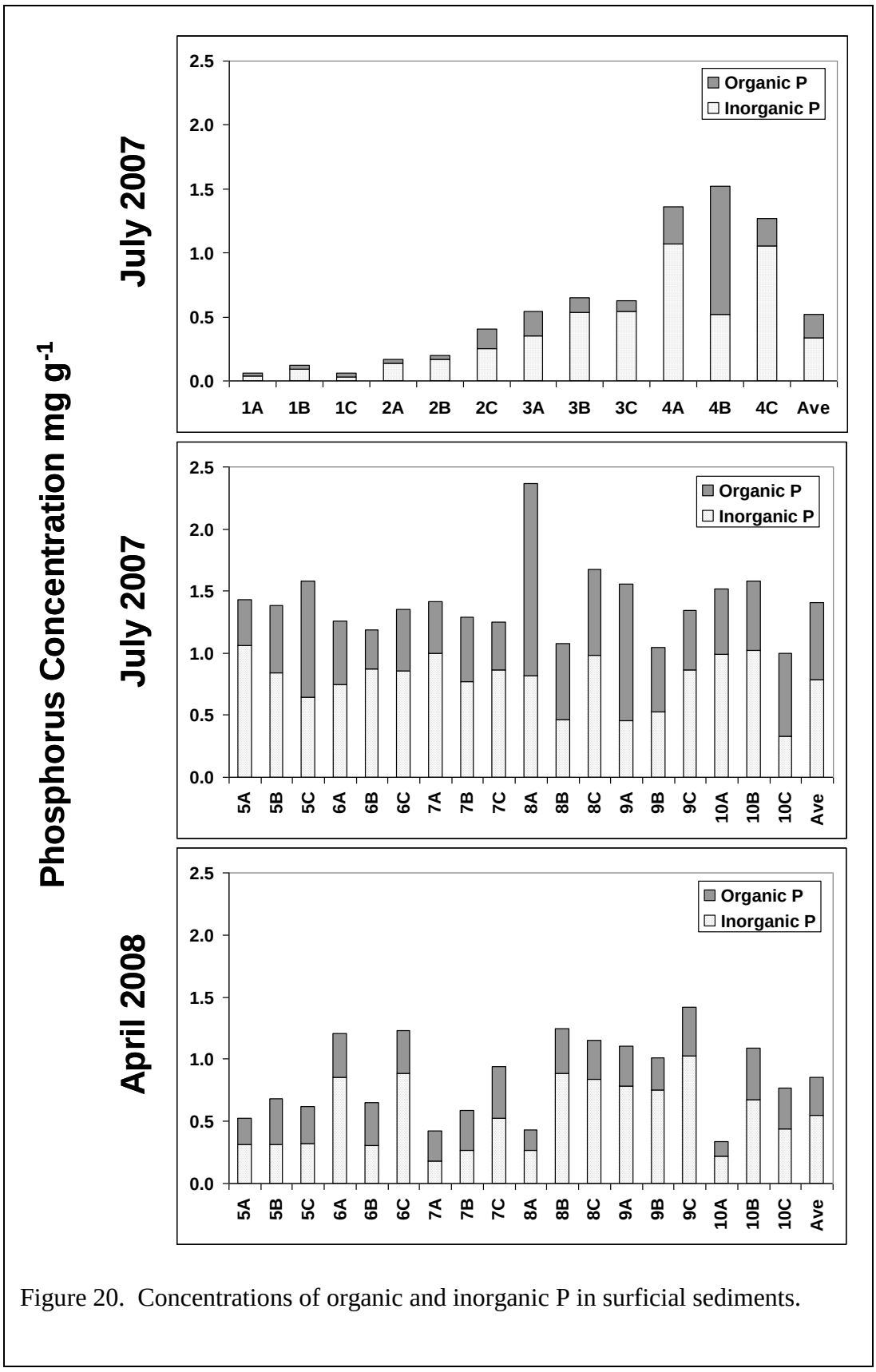


Figure 20. Concentrations of organic and inorganic P in surficial sediments.

SOLID PHASE ANALYSES – VERTICAL PROFILES

The vertical profiles of sediment P, loss on ignition (LOI) and carbon showed variable degrees of change from surface to deep horizons (Figure 21). Site A had little vertical change in inorganic and total P, with whole core averages that were quite well constrained. Site A organic P was a relatively constant 0.25±0.03 mg g^{-1}. Although site B had a considerable change from top to bottom in total P, largely driven by changes in the inorganic P concentration, organic P concentrations averaged 0.22±0.04 mg g^{-1}, similar to Site A. The large increase in inorganic P at Site B likely is a function of the post-depositional mobility of Fe and P in pore water (Carignan and Flett 1981; Cornwell 1987; Chambers and Odum 1990; Bryner 2000), with the dissolution of iron oxides leading to iron sulfide formation. Iron monosulfide minerals and pyrite adsorb inorganic P much less than iron oxides, and conversion of oxides to sulfides leads to a buildup of pore water P. Upward diffusion can result in resorption of P onto iron oxides in more oxidizing sediment horizons.

Table 6. Vertical profile data. LOI is loss on ignition, TP is total P, IP is inorganic P and OP is organic P, determined as the difference between TP and IP.

Core	Depth Interval	Bulk Density g cm^{-3}	LOI	C %	N	TP	IP mg g^{-1}	OP	^{210}Pb dpm g^{-1}
	0.0-2.5	0.282	22.4	10.4	0.70	0.71	0.39	0.33	4.71±0.20
	2.5-5.0	0.369	17.3	7.2	0.54	0.63	0.35	0.28	4.58±0.19
	5.0-7.5	0.489	14.4	6.4	0.50	0.64	0.38	0.26	5.11±0.26
	7.5-10.0	0.474	14.0	5.7	0.48	0.61	0.39	0.21	4.14±0.17
	10-15	0.440	14.9	6.2	0.50	0.59	0.37	0.22	4.03±0.23
	15-20	0.421	15.5	7.0	0.52	0.64	0.37	0.27	3.95±0.21
A	20-25	0.461	15.1	6.8	0.54	0.64	0.39	0.25	3.66±0.11
	25-30	0.442	14.3	6.3	0.51	0.63	0.41	0.22	3.51±0.09
	30-40	0.411	15.1	6.4	0.52	0.66	0.44	0.21	2.82±0.14
	40-50	0.381	16.0	7.1	0.54	0.63	0.39	0.24	3.13±0.16
	50-60	0.343	18.0	7.9	0.57	0.67	0.39	0.28	5.13±0.21
	Ave	0.410	16.1	7.0	0.54	0.64	0.39	0.25	
	SD	0.062	2.3	1.2	0.06	0.03	0.02	0.03	
	0.0-2.5	0.516	17.7	5.4	0.42	0.91	0.69	0.22	2.72±0.20
	2.5-5.0	0.481	14.3	5.7	0.42	0.89	0.63	0.26	4.46±0.22
	5.0-7.5	0.443	14.7	5.6	0.42	0.75	0.49	0.26	4.83±0.22
	7.5-10.0	0.493	14.8	5.6	0.40	0.63	0.38	0.26	3.68±0.10
	10-15	0.563	12.8	4.4	0.35	0.57	0.32	0.25	3.42±0.08
	15-20	0.495	11.9	4.5	0.37	0.60	0.35	0.24	3.61±0.16
B	20-25	0.447	12.9	4.7	0.35	0.56	0.32	0.24	3.30±0.11
	25-30	0.471	13.2	5.6	0.37	0.51	0.31	0.20	2.62±0.09
	30-40	0.520	11.6	4.3	0.31	0.53	0.32	0.20	2.26±0.06
	40-50	0.565	10.4	3.9	0.28	0.50	0.32	0.18	1.39±0.08
	50-60	0.557	10.1	3.8	0.28	0.48	0.34	0.14	1.37±0.07
	Ave	0.505	13.1	4.9	0.36	0.63	0.41	0.22	
	SD	0.044	2.1	0.7	0.05	0.15	0.13	0.04	

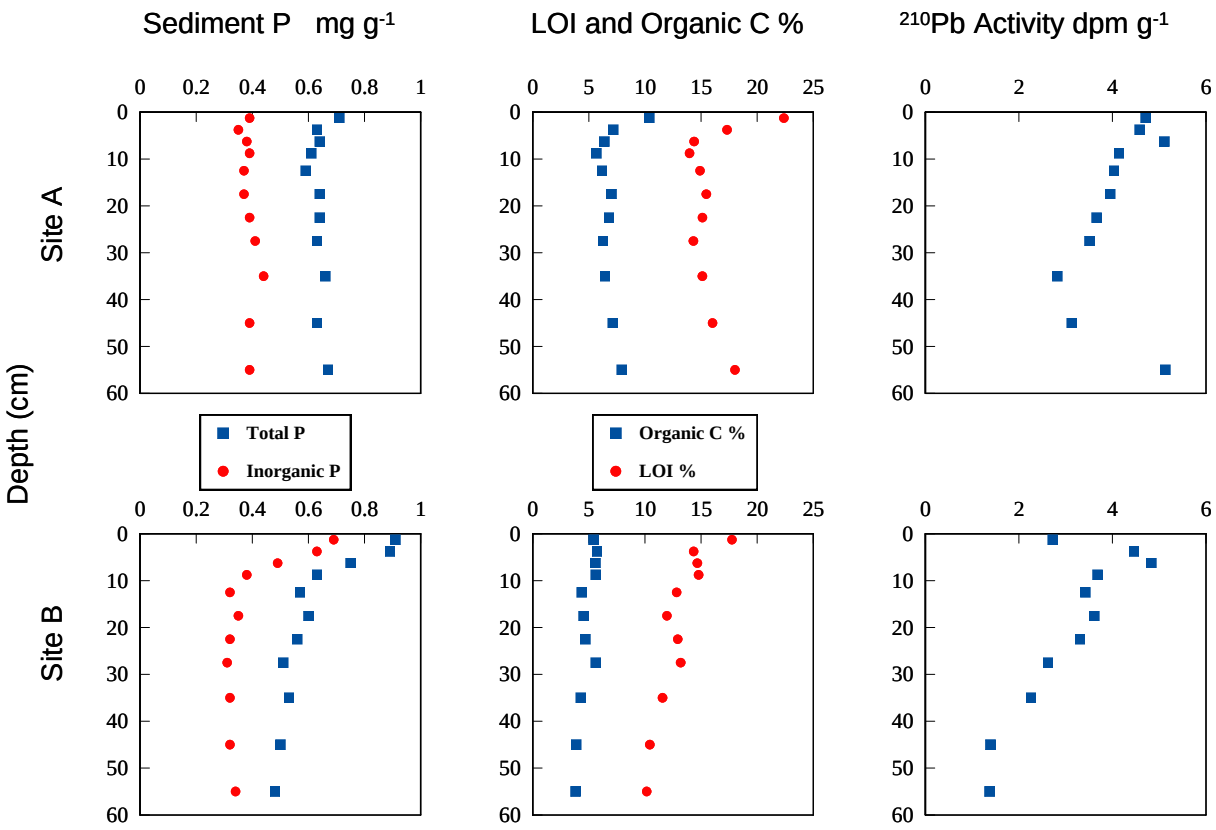


Figure 21. Vertical profiles of total P, inorganic P, loss on ignition, organic C, and ^{210}Pb activity.

Loss on ignition and organic C concentration profiles have a similar shape and a regression of the two parameters showed that LOI was 2.4 times as high as organic C, similar to the near-surface samples. Organic C averaged 7.0±1.2% in A and 4.9±0.7% in B, with A showing a two-fold enrichment in the near-surface sample. Total N concentrations averaged 0.54±0.06 and 0.36±0.05% for A and B respectively (Figure 22).

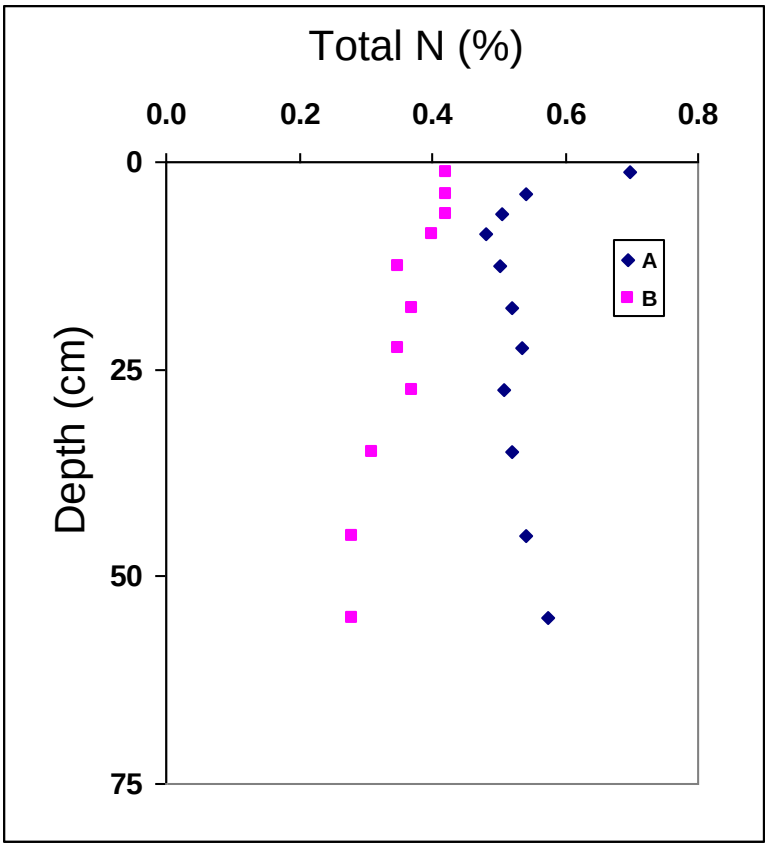


Figure 22. Vertical nitrogen concentration profile.

The profiles of ^{210}Pb did not show a simple exponential decline (Figure 21). In core A, the activity of ^{210}Pb decreased over the top 30 cm, but had a deep increase in activity. Core B had a subsurface peak, with exponential character at greater depth. The profiles of (Velinsky et al. 2010) were much more regular and their rates were corroborated with ^{137}Cs. Both of our sites had a large number of burrowing fiddler crabs and some degree of bioturbation was likely. The effect of such mixing is to create an apparent higher accretion rate. While core B had an inventory of ^{210}Pb (36 dpm cm^{-2}) about 50% higher than atmospheric inputs (~25 dpm cm^{-2}(Kim et al. 2000), core A had an inventory (≥60 dpm cm^{-2}) 2.5 times the atmospheric input. Higher than expected inventories may be considered focusing of materials into the site; these data are similar to other dated cores in the Murderkill marsh (Velinsky et al. 2010).

The profile of excess ^{210}Pb, the ^{210}Pb not supported by in situ generation, in an unmixed sediment profile may be described:

$$A = A_0 e^{(-\lambda x/\omega)}$$

where A is the activity (dpm g^{-1}) at depth x (cm), λ is the decay constant, and ω is the sediment accretion rate (cm yr^{-1}). This formulation is the **c**onstant **i**nitial **c**oncentration

model ("CIC") of ^{210}Pb-based sedimentation. It depends on 1) constant input fluxes of both sediment and excess ^{210}Pb, 2) no post depositional mobility of ^{210}Pb relative to sediment particles, and 3) no sediment mixing by biota or physical processes. To apply this model, the equation is log transformed:

$$\ln A = \ln A_0 - (\lambda x/\omega)$$

We used cumulative mass instead of depth for the calculation; this removed changes in bulk density as an artifact of depth. Figure 23 shows the plot of the two cores as a function of cumulative mass, the latter calculated from bulk density. Sediment accumulation rates were 5,227 and 3,888 g m^{-2} y^{-1} for A and B respectively. Mixing would create an artifact of high accretion rates; these rates are 2-3 times as high as estimates by (Velinsky et al. 2010).

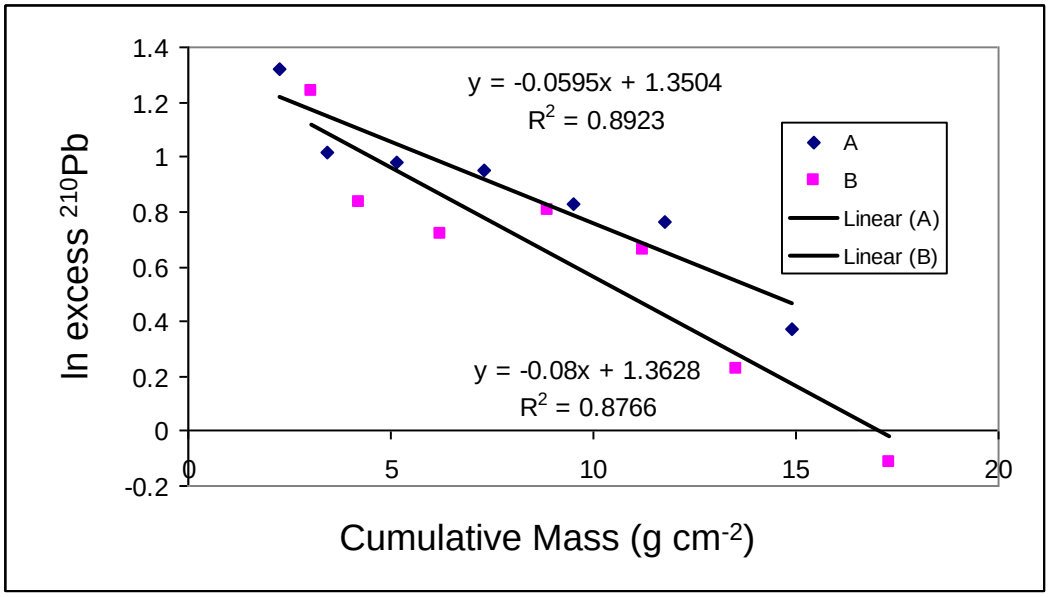


Figure 23. Plot of the natural log of excess ^{210}Pb versus cumulative mass.

CONCLUSIONS

The nitrogen cycling data in this report is best understood in a mass balance framework (Figure 23). Nitrogen loading from point and non-point sources was not determined in this study, but other investigators have been developing this information. Our sediment water exchange experiments have determined on two occasions the production/consumption of inorganic nutrients, oxygen and N_2-N at the soil-water interface in Murderkill wetlands. The role of plant uptake from soil and the potential role of benthic algae on uptake of nitrogen from soil and overlying water have not been assessed. In addition, groundwater flow paths that remove/introduce N species to the marsh are no known. The value of these wetlands to water quality on an annual basis is the sum of burial and denitrification; seasonal storage of N in plant material is also a shorter-term water quality benefit.

As described before, the burial rates of N from these two study sites are likely high because of the activities of abundant fiddler crab communities which mix tracers like ^{210}Pb rapidly into the sediment. We can also calculate a burial rate based on bulk density and an assumed 4 mm y^{-1} accretion rate. The (Velinsky et al. 2010) study shows a coherent chronology for two radionuclides (^{210}Pb and ^{137}Cs) at 4 sites (Table 6), with accretion rates considerably lower than calculated in this study. Annual N burial rates ranged from 10-23 g N m^{-2} y^{-1}. For our purposes here, we will use Velinsky et al.'s nitrogen burial estimates. On an annual basis, nitrogen burial rates are virtually identical to the rates of denitrification.

The largest aqueous N fluxes observed were the sediment uptake of NO_x (nitrate + nitrite) and the release of N_2 gas, with average NH_4^+ effluxes being low or negative (Figure 24). This study does not include cold season fluxes; in winter fluxes are likely to be much lower because of low rates of microbial activity. Velinsky et al. (2010) cite data by Ullman that suggest a five fold range in monthly N loading; the data are converted to an hourly basis in Figure 25. Both denitrification and N burial estimates are between high and low N loading estimates; ***denitrification and N burial represent the main N "sinks" in the Murderkill ecosystem and can account for most, if not all of the point and non-point source N inputs.***

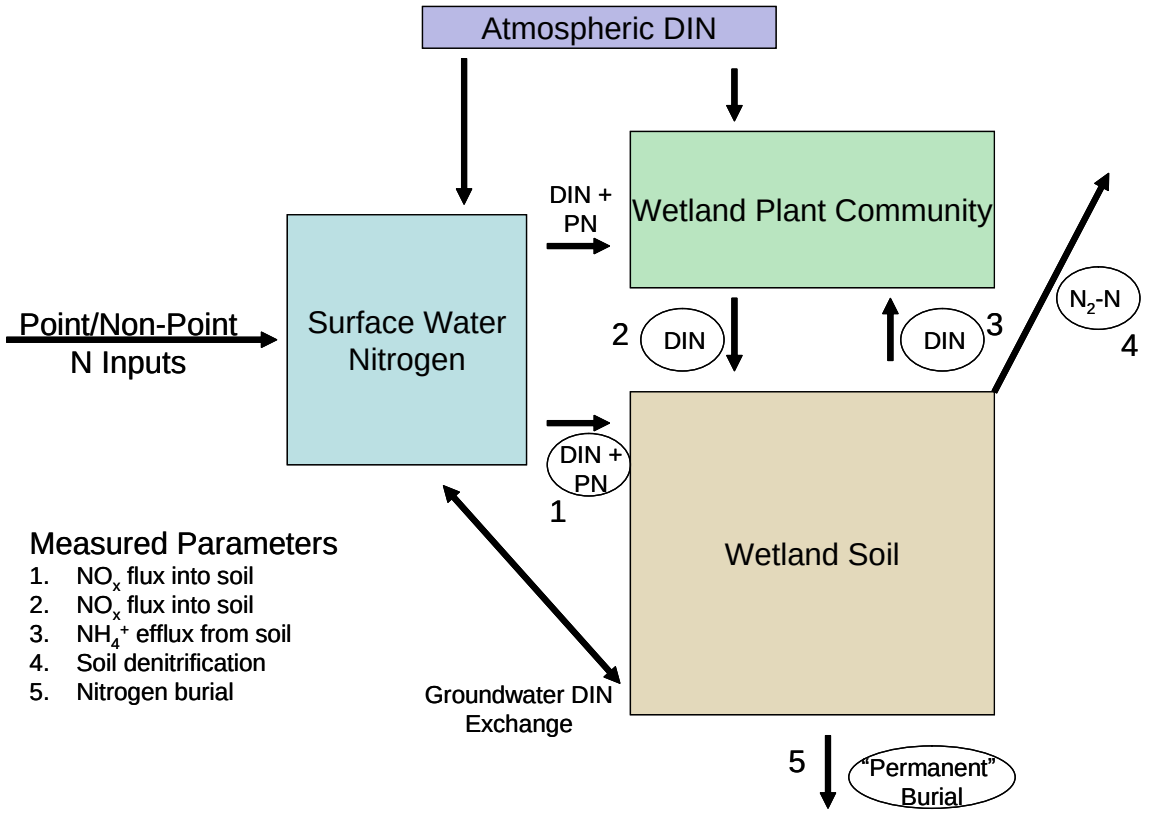


Figure 24. Simplified diagram of marsh nitrogen cycle, emphasizing fluxes measured in this project. We have data for circled fluxes. Net fluxes of dissolved inorganic nitrogen into the soil, primarily nitrate plus nitrite (NO_x), have both direct surface water inputs (1), decomposition inputs (2) and groundwater inputs/export (not measured in this study). The surface of the soil interacts with the overlying water (when flooded) and the main inorganic nutrient flux is DIN as NH_4^+ (3) and denitrification (4). Permanent burial (5) was assessed using geochronology (Velinsky et al. 2010) and nitrogen concentrations; slow organic matter decomposition may decrease the apparent N burial term to a small degree. From a water quality perspective, both denitrification (4) and burial (5) are key to minimizing the effect of nutrients to receiving waters.

Table 7. Annual N cycling estimates.

Site	Units	Site A		Site B	
P concentration	mg g^{-1}	0.64±0.03		0.63±0.15	
N concentration	mg g^{-1}	5.4±0.06		3.6±0.05	
^{210}Pb-Based Sedimentation	Mass (g m^{-2} y^{-1})	5,227		3,888	
	Accretion (cm y^{-1})	1.27		0.77	
	P (g m^{-2} y^{-1})	3.3		2.4	
	N (g m^{-2} y^{-1})	28		14	
4 mm y^{-1} Based Sedimentation	Mass (g m^{-2} y^{-1})	1,640		2,020	
	P (g m^{-2} y^{-1})	1.0		1.5	
	N (g m^{-2} y^{-1})	9		7	
Annual Denitrification (143±61 μmol m^{-2} h^{-1})	N (g m^{-2} y^{-1})	18		18	
Velinsky et al. (2010) burial		MK-1	MK-2	MK-3	MK-4
	Mass (g m^{-2} y^{-1})	2,000	1,300	1,400	1,700
	P (g m^{-2} y^{-1})	2	1.5	2	3
	N (g m^{-2} y^{-1})	18	17	23	10

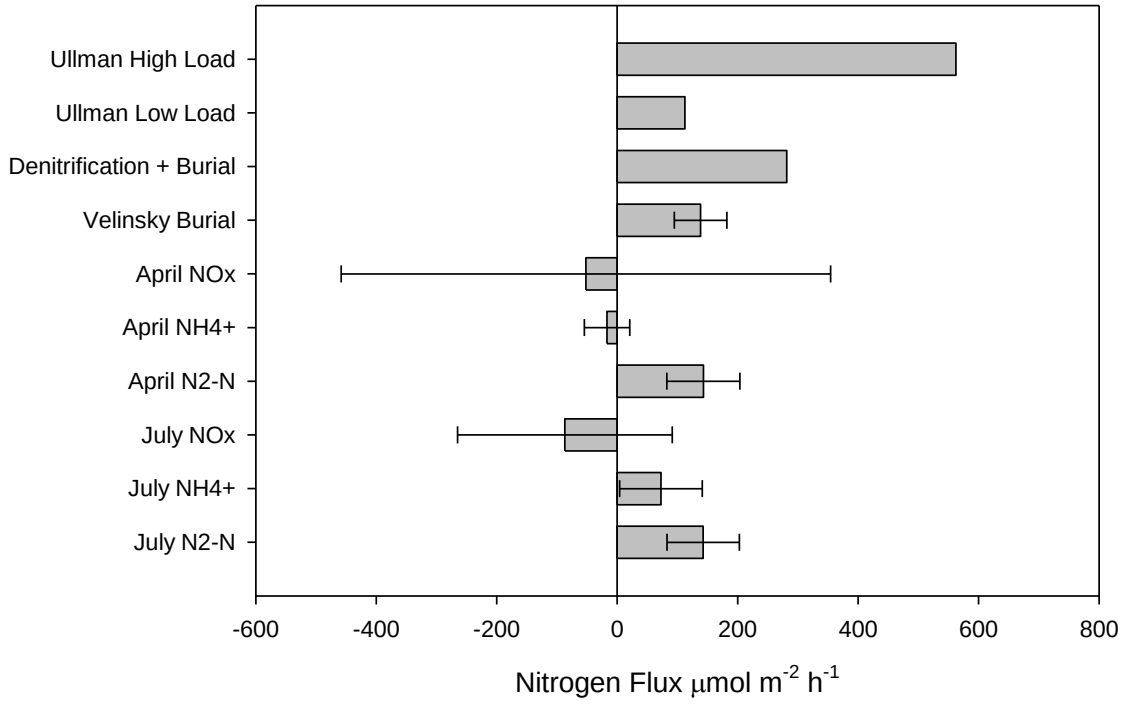


Figure 25. Net nitrogen fluxes. The loads and burial numbers are from (Velinsky et al. 2010) and are transformed to an hourly basis. Error bars are standard deviations for the nutrient fluxes (N = 12 for each bar) and for the nitrogen burial (N = 4).

SECTION II: WATER COLUMN RESPIRATION

Introduction

Background: Wetland Biogeochemical Processes

Tidal marshes are variously sinks or sources of biogeochemical constituents. Considerable interest in tidal marsh exchange with adjacent waters was developed as part of an outwelling hypothesis in which dissolved and particulate organic matter was exported from marshes (Nixon 1980; Childers et al. 2000). The organic matter exported from tidal marshes can contribute to elevated water column respiration rates which could vary seasonally due to water temperature and lability of the organic matter. The bacteria responsible for the consumption of oxygen in the water column can be both free living and attached to particulate substrate. Tidal induced draining of marshes can release reduced chemical species (hydrogen sulfide) into the water column which can also add to the demand for oxygen in the water column.

A recent study of the Monie Bay brackish marsh system suggested temperature (Apple et al. 2006) and the lability of organic matter (Apple et al. 2007) were major controls on rates of bacterial respiration and production. Comparison of contrasting nutrient regimes in sub-sections of this National Estuarine Research Reserve suggested that nutrient availability was not the dominant control.

Overview of Sampling Plan

The goal of this project was to provide data on the rate of oxygen consumption in the water column of the Murderkill River. Our previous flux work has shown that, at least in summer, there were high rates of water column respiration which were higher than the standard BOD_5 measurements made by DNREC. The rates that we measured were from our (water only ~1μm filtered) water column blank incubations used for correcting our flux measurements for water column activity. The standard BOD_5 measurements are a longer term BOD (Biological Oxygen Demand) measured over a 5 day period and could underestimate the breakdown of very labile dissolved organic matter.

We measured short term raters of dark respiration on the order of 4 to 8 hours. We sampled whole water during the DNREC water quality sampling cruises and coordinated sampling with Jonathan Sharp's group at the University of Delaware to ensure that we sample the same water mass for both the respiration and production measurements. In addition to our oxygen time course measurements we also collected samples for ammonium and nitrate to determine how much of the oxygen demand was due to water column nitrification. Samples for dissolved inorganic carbon (DIC) were collected at the beginning and the end of the time course sampling in July 2008 and sent to the University of Delaware for analysis. The DIC measurement were used to determine to what extent chemical oxygen demand might play a role in the overall consumption of oxygen in the water column.

Monitoring Parameters

The monitoring parameters are outlined in table 7.

Table 8. Parameters Outline

Water Column Respiration Measurements

A. Solutes: dissolved O_2, soluble reactive NH_4^+, NO_3^-
B. Surface water samples unfiltered
C. Replication: 1 station will be replicated
D. Incubation time: 4-8 hours
E. 60 ml BOD bottles: ambient water temperature

Sampling and Experimental Procedures

Field Sampling – Water Samples

Surface water samples were collected in 4 L polyethylene bottles at each site and transport to the lab. Ambient water temperature was maintained as close as possible during transport.

Water Column Respiration Protocols--Laboratory

We examined a time course of high precision oxygen measurements to determine rates of water column respiration. Our approach using membrane inlet mass spectrometry has been successfully applied in marsh ecosystems (Apple et al. 2006)); the final analysis uses the same mass spectrometer utilized by that study.

Water samples were aerated for 30 min to maintain oxygen concentrations near saturation. We measured time courses of dissolved oxygen, argon, ammonium, and nitrate. Water samples were mixed and then siphoned into 60 ml BOD bottles and capped. A total of 6 BOD bottles were filled at each station and incubated in the dark at *in situ* temperatures. A water jacketed incubator was used to maintain *in situ* temperatures for the duration of the incubation. All incubations were conducted in the dark.

Water samples were collected by gravity and solute samples were syringe filtered using a 0.45 μm disposable filter unit. Samples for ammonium and nitrate were preserved by freezing until chemical analysis. Gas (O_2, Ar) samples were collected in 7 mL ground-

glass stoppered vials and preserved with mercuric chloride and stored at near ambient temperatures after immersion in water to prevent drying of the ground glass seal. We have successfully preserved such samples for time periods in excess of 3 weeks. Water column dissolved oxygen, temperature, salinity, and pH were measured in the field by DNREC personnel at the time of water collection.

Analytical Procedures

Solutes

Solute and gas analyses are summarized in Table 8. Nutrient analyses will be on frozen samples. We replicated a minimum of 10% of all dissolved and gas analyses.

Table 9. Dissolved Constituent Analysis.

Analyte	Reference	Description
NH_4^+	(Parsons et al. 1984)	Automated Phenol/hypochlorite coloroimetry
NO_3^-	(Parsons et al. 1984)	Automated colorimetric analysis (d.l. < 0.03 mg L^{-1})
dissolved O_2, Ar	(Kana et al. 1994)	mass spectrometry

Results and Discussion

Core blanks

Our sediment-water exchange measurements are normally conducted on 2 to 3 replicate cores and 1 blank core containing only bottom water from a given site. These blank cores are stirred in the same manner as the flux cores and have approximately the same water volume. These blank incubations are used to correct for changes in O_2 consumption and nutrient concentration that are due solely to the activity of bacteria or phytoplankton in the water column. We typically filter our water bottom water through a 1 μm filter prior to our flux incubations in order to reduce any water column effect from phytoplankton. The rates for our water column blanks from July 2007 and April 2008 are shown in table 1.

We measured rates of respiration in our core blanks in July 2007 that were typically 6 fold higher than the surface water long term biological oxygen demand (LTBOD) measurements (range of 0.5-1.0 mg O_2 $l^{-1}d^{-1}$) made in July 2007 at stations in close proximity to our sediment flux coring sites. In April 2008, we made additional measurements of water column respiration using small bottle incubations of unfiltered surface water from each site. The April 2008 bottle incubations were similar to the core blanks at most sites with the exception of the 2 upstream end members. Stations 9 and 10 both showed 3 to 4 fold higher respiration in the core blanks compared to bottle incubations. This discrepancy in rates might be caused by differences between surface and bottom water at the 2 upstream sites; bottle incubations were conducted on surface water.

Table 10. Water column respiration rates from blank core incubations July 2007 and April 2008.

			Depth	Water Column Respiration O_2 mg l^{-1} d^{-1}		
ID	Lat N	Long W	m	July 2007 Core Blanks	April 2008 Core Blanks	April 2008 Bottle
1	39°02.854	75°23.613	2.9	6.83	n.d.	n.d.
2	39°01.253	75°25.467	3.4	6.66	n.d.	n.d.
3	39°00.592	75°26.383	2.8	9.09	n.d.	n.d.
4	39°00.718	75°27.699	1.5	6.61	n.d.	n.d.
5	39°03.021	75°23.484	0.2	7.36	1.64	1.14
6	39°02.778	75°23.777	0.2	3.72	2.04	2.36
7	39°01.965	75°24.638	0.3	7.05	1.29	1.05
8	39°00.468	75°26.388	0.9	4.65	1.56	1.16
9	39°00.729	75°27.065	0.7	8.26	2.54	0.91
10	39°00.717	75°27.761	0.7	8.98	3.65	0.82

Short term bottle incubations

The LTBOD measurements may not capture elevated short term (hours) rates of metabolism that are supported by very labile organic carbon that could be supplied from the wetland on tidal cycles. The water column respiration measurements we conducted in this study were designed to capture short term rates of metabolism on the order of 6-8 hours. Our short term rates of water column respiration are shown in table 2. These samples were collected by DNREC personnel as part of their routine water quality transect of the Murderkill River on July 7, 2008 and November 12, 2008. The rates measured in July of 2008 were over 3 fold lower than the rates measured in July of 2007. The difference between rates between July 2007 and July 2008 data could be related to the sample collection depth. The surface water may have a lower BOD than the bottom water due to resuspension of sediments.

Table 11. Rates of short term water column respiration from the DNREC water quality survey from July and November 2008.

Station ID	Sample Depth	Water Column Respiration O_2 mg l^{-1} d^{-1}	
		July 2008	Nov. 2008
206101	surface	1.85	0.34
206131	surface	1.32	0.29
206141	surface	1.57	0.27
206711	surface	1.61	0.29
206231	surface	1.26	0.29
206091	surface	1.95	0.22
206081	surface	1.79	0.31

Chemical oxygen demand could cause high rates of BOD in the Murderkill River through the oxidation of H_2S, CH_4 or other reduced species released from marsh drainage. During our July 2008 incubations we included dissolved inorganic carbon (DIC)

measurements in our time course incubations. The rates of DIC production should be similar to the consumption of O_2 on a molar basis if the O_2 demand is driven primarily by heterotrophic process. Table 3 shows the rates of water column respiration and DIC production for all sites sampled in July 2008. Most sites showed similar rates of O_2 consumption and DIC production indicating that most of the respiration was probably due to heterotrophic breakdown of organic carbon and not chemical oxygen demand. The respiratory quotient (RQ) for the decomposition of biochemical compounds is in the range of 0.67-1.24 (del Giorgio and Williams 2005). Most of the stations fall in the normal RQ range with the exception of stations 206131 and 206141 (Figure 2). There is little evidence to support chemical oxygen demand in the water column with all RQ values above 0.67. Aeration of the water column samples prior to our respiration experiments was required in July 2007 due to low *in situ* O_2 concentrations. This aeration step would likely cause an underestimate of the importance of chemical oxygen demand with some of the reduced species being oxidized prior to our incubation. Stations 206131 and 206141 do have high values for RQ with about twice as much CO_2 produced for each O_2 consumed.

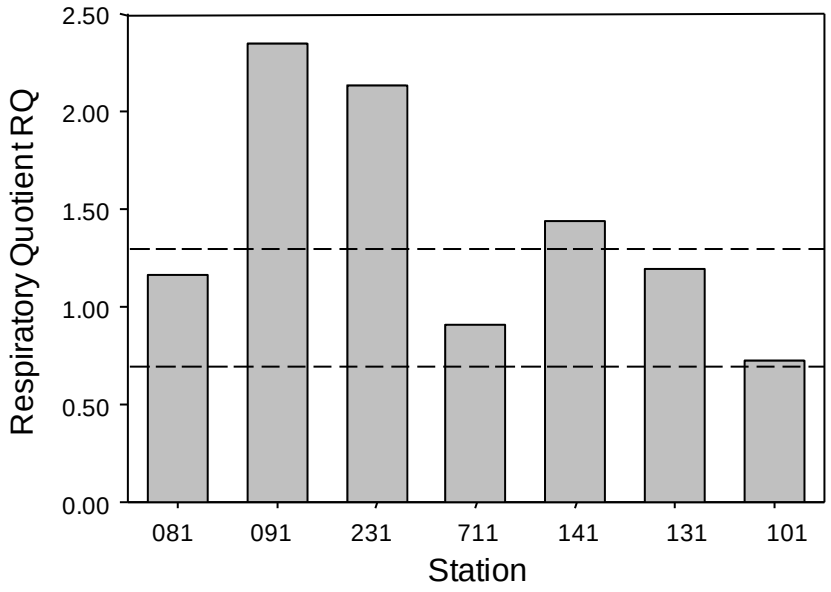


Figure 26. Respiratory quotient from surface water samples collected July 7, 2008. Dashed lines represent normal range of for the decomposition of organic compounds. Values below 0.67 would suggest chemical oxygen demand.

The rates of water column nitrification are shown in tables 3 and 4 for July and November 2008 respectively. We calculated the percentage of O_2 consumed in the water column by nitrification by assuming a stoichiometry of $2O_2$ to oxidize 1 mole of NH_4^+. In July 2008 nitrification was responsible for 3% to 46% of the total respiration. The July 2008 rates of respiration were 5 to 10 fold lower than in July but the process of nitrification was responsible for close 50% of the O_2 consumption during both sampling times. A similar proportion of O_2 consumption (~50%) via nitrification was found for the Seine River (France)(Garnier et al. 2001). The maximum rates of water column

respiration for the Seine River were at least 2 fold higher than the Murderkill River and water column NH_4^+ concentrations were ~ 100 μM. The high NH_4^+ concentrations in the Seine River have been identified as a major source of O_2 demand. The Muderkill River is a turbid, probably net heterotrophic system similar to the Seine and increases in NH_4^+ concentrations would likely drive higher rates of water column respiration.

Table 12. Rates of water column respiration, nitrification and DIC production from surface water samples collected July 7, 2008.

July 2008	Water Column Respiration	DIC	Nitrification	Water Column NH_4^+	O_2 consumed Via Nitrification
Station ID	μmoles l^{-1} h^{-1}	μmoles l^{-1} h^{-1}	μmoles l^{-1} h^{-1}	μM	%
206101	2.41	1.74	0.19	2.56	15.63
206131	1.72	2.06	0.24	8.62	27.36
206141	2.04	2.94	0.36	15.01	34.92
206711	2.09	1.90	0.15	16.74	14.14
206231	1.63	3.49	0.38	21.20	46.06
206091	2.54	5.97	0.04	6.48	3.21
206081	2.33	2.68	0.22	2.56	16.18

Table 13. Rates of water column respiration and nitrification from surface water samples collected November 12, 2008.

November 2008	Water Column Respiration	DIC	Nitrification	Water Column NH_4^+	O_2 consumed Via Nitrification
Station ID	μmoles l^{-1} h^{-1}	μmoles l^{-1} h^{-1}	μmoles l^{-1} h^{-1}	μM	%
206101	0.44	n.d.	n.s.	5.6	--
206131	0.38	n.d.	0.05	5.1	24.84
206141	0.35	n.d.	n.s.	8.9	--
206711	0.38	n.d.	0.11	9.7	60.62
206231	0.38	n.d.	n.s.	42.6	--
206091	0.28	n.d.	n.s.	20.0	--
206081	0.40	n.d.	0.12	20.4	55.78

n.d. - No data collected
n.s. – No significant regression

Summary

The Murderkill River water column respiration rates measured in April and July 2008 averaged 1.2+/-0.5 and 1.5+/-0.3 respectively. The rates measured in our flux core blanks from July 2007 averaged 6.4+/-1.7 mg O_2 l^{-1} d^{-1}. These are all high rates of water column respiration compared to maximum published literature rates of ~7.6 mg O_2 l^{-1} d^{-1}(del Giorgio and Williams 2005). Our core blanks incubate bottom water and are meant to be a correction for our sediment flux incubations only and may not represent a true measure of *in situ* water column respiration. Nitrification is an important process consuming O_2 in the water column of the Murderkill River and at times accounts for 50% of the O_2 consumption. The RQ values calculated from our data do not suggest that these high rates of respiration were driven primarily by heterotrophic processes and not chemical oxygen demand.

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